BULLETIN OF THE RESEARCH COUNCIL OF ISRAEL

Section A
CHEMISTRY

Bull. Res. Counc. of Israel. A. Chem.

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3. TAYLOR, G. I., 1932, *Proc. roy. Soc.*, A138 41.

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4. JACKSON, F., 1930, *Thermodynamics*, 4th ed., Wiley, New York.

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THE KINETICS OF COMPETITIVE, CONSECUTIVE, SECOND-ORDER REACTIONS INVOLVING ONLY ONE PRIMARY REACTING SPECIES

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ABSTRACT

The reaction scheme, $A + A \rightarrow B + D$ followed by $A + B \rightarrow C + D$, is considered for a wide range of values of R, the ratio of the rate constants of the two reactions. The value of R is best determined by comparing the relative concentration of the intermediate B during the course of the reaction with a series of standard curves drawn for particular values of R. The rate constants are then evaluated from the slope of the straight line obtained by applying "corrections" to the usual second-order kinetic plot. These corrections which are functions of R are given in graphical form. A modification of the method, for use when the concentration of the intermediate B cannot be measured, is described and compared with the time-ratio method of Frost and Schwemer.

INTRODUCTION

A kinetic study of a chemical reaction believed to follow a particular reaction mechanism is normally carried out with two objects in view, to verify that the kinetics are consistent with the proposed reaction mechanism and to evaluate the various rate constants involved. The purpose of the present paper is to provide a simple method for attaining these objects in the case of competitive, consecutive, second-order reactions involving only one primary reacting species, as exemplified by the equations

and
$$A + A \xrightarrow{k_1} B + D$$
$$A + B \xrightarrow{k_2} C + D.$$
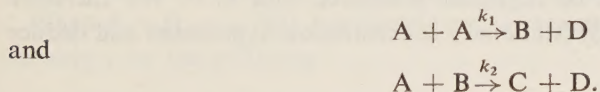
Our interest in such reactions was aroused when we found[1,2] that solutions of sodium hypobromite decompose in this manner to give bromate and bromide, bromite appearing as an intermediate. Such reactions are comparatively rare and, as far as we know, have not been discussed elsewhere in the literature, although methods have been described[3-8] for determining the rate constants of the corresponding reaction involving two primary reacting species, namely

and
$$A + B \rightarrow C + E$$
$$A + C \rightarrow D + E.$$
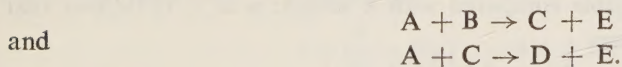
Many of these methods involve either approximations[4], or a suitable choice of the relative initial concentrations of the reactants[5,6], or both[7]. None of these methods

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can be applied directly when there is only one reacting species. In addition, a number of procedures have been described for solving the simpler problem of determining the ratio of the rate constants of the two reactions for the case of both one[1] and two[9,10] primary reacting species.

The second-order rate equations for our reaction scheme will be

$$- d[A]/dt = 2 k_1[A]^2 + k_2[A][B]$$

and

$$d[B]/dt = k_1[A]^2 - k_2[A][B]. \tag{1}$$

It is convenient to introduce reduced concentrations x and y and a reduced time τ defined by

$$x = [A]/[A]_0, \quad y = [B]/[A]_0, \quad \text{and} \quad \tau = t[A]_0,$$

where $[A]_0$ is the initial concentration of the reactant A. The above rate equations then take the form

$$- dx/d\tau = k_1(2x^2 + xy/R) \tag{2}$$

and

$$dy/d\tau = k_1(x^2 - xy/R), \tag{3}$$

where R is defined by

$$R = k_1/k_2. \tag{4}$$

Furthermore, assuming the initial concentrations of B and C to be zero, we see that at any moment

$$[A] + 2[B] + 3[C] = [A]_0$$

from which it follows that

$$x + 2y = \{ 1 - 3[C]/[A]_0 \} = u \text{ (say)}. \tag{5}$$

We first consider the case when R is extremely small; the value of y will then remain extremely small throughout the reaction so that (except for a short induction period) the value of $dy/d\tau$ will be negligible compared with $k_1 x^2$. We therefore put $dy/d\tau$ equal to zero in Eq. (3) (stationary concentration hypothesis) and deduce that

$$xy/R = x^2.$$

On introducing this result into Eq. (2) we obtain

$$- dx/d\tau = 3 k_1 x^2$$

which on integration gives

$$1/x = 3 k_1\tau + 1, \tag{6}$$

the usual equation for a single-step second-order reaction. Furthermore, under these circumstances y is negligible compared with x so that $u = x$. It follows that Eq. (6) can be written in the form

$$1/u = 3 k_1\tau + 1.$$

Clearly in this special case the value of k_1 can be obtained directly from the slope of the experimental straight-line graph obtained by plotting either $1/x$ or $1/u$ against τ.

We shall now consider the more general case when R is no longer extremely small; our method of evaluating the rate constants k_1 and k_2 consists of determining R and

k_1 and then calculating k_2 from Eq. (4). The course of the chemical reaction will usually be followed by carrying out a series of measurements of either the concentration of the reactant A, thus determining x, or the concentration of the final product C, thus determining u. (A third possibility, that of following the course of the reaction by measuring the concentration of the common product D has not been considered in detail, though a method similar to that described below could also be worked out for this case.) Furthermore it may or may not be possible to measure the — possibly small — concentration of the intermediate B (thus determining y) depending on whether or not a suitable analytical procedure is available. We consider first the case when such measurements of y are available.

DETERMINATION OF R FROM CONCENTRATION OF INTERMEDIATE B

An extremely simple method[1] of determining R is to measure the concentrations of A and B when the intermediate B has its maximum concentration, i.e. when $d[B]/dt = 0$. It follows from Eqs. (1) and (4) that R will be equal to the ratio $[B]/[A]$ at this stage of the reaction. However, this simple method has two serious disadvantages; firstly it is based on experimental results obtained at only one particular stage of the reaction and secondly a considerable error may be introduced into the calculated value of R owing to the difficulty in determining the exact stage of the reaction at which the concentration of the intermediate B is a maximum. In order to avoid these disadvantages, we adopt the standard procedure of dividing Eq. (3) by Eq. (2), thus obtaining the homogeneous differential equation

$$dy/dx = (y - Rx)/(y + 2\,Rx).$$

The solution of this equation takes different forms according to the value of R.

When $R < (1 - \sqrt{3}/2)$, it is convenient to express x and y in terms of an auxiliary variable v by the relations

$$\log x = \left(l - \frac{1}{2}\right)\log\left(v - \frac{1}{2}\right) - \left(l + \frac{1}{2}\right)\log\left(v + \frac{1}{2}\right)$$

$$- \left[\left(l - \frac{1}{2}\right)\log\left(v_0 - \frac{1}{2}\right) - \left(l + \frac{1}{2}\right)\log\left(v_0 + \frac{1}{2}\right)\right] \tag{7}$$

and

$$y = x\left[\frac{1}{2} - R - v\left(1 - 8R + 4R^2\right)^{\frac{1}{2}}\right] \tag{8}$$

where the parameter l is given by

$$l = \left(\frac{1}{2} + R\right)\left(1 - 8R + 4R^2\right)^{-\frac{1}{2}} \tag{9}$$

and v decreases from its initial value v_0 at the beginning of the reaction, given by

$$v_0 = \left(\frac{1}{2} - R\right)\left(1 - 8R + 4R^2\right)^{-\frac{1}{2}},$$

to its final value of $\frac{1}{2}$ at the end of the reaction.

When $(1 - \sqrt{3}/2) < R < (1 + \sqrt{3}/2)$, we express x and y in terms of a second auxiliary variable θ by the relations

$$\log x = \log \cos \theta - m\theta - (\log \cos \theta_0 - m\theta_0) \tag{10}$$

and

$$y = x\left[\frac{1}{2} - R + \left(-\frac{1}{4} + 2R - R^2\right)^{\frac{1}{2}} \tan \theta\right] \tag{11}$$

where the parameter m is given by

$$m = 0.4343\left(\frac{1}{2} + R\right)\left(-\frac{1}{4} + 2R - R^2\right)^{-\frac{1}{2}}$$

and θ increases from its initial value θ_0 at the beginning of the reaction, given by

$$\tan \theta_0 = \left(R - \frac{1}{2}\right)\left(-\frac{1}{4} + 2R - R^2\right)^{-\frac{1}{2}}$$

to its final value of $\pi/2$.

Finally, when $R > (1 + \sqrt{3}/2)$, we express x and y in terms of a third auxiliary variable w by the relations

$$\log x = \left(l - \frac{1}{2}\right)\log\left(w + \frac{1}{2}\right) - \left(l + \frac{1}{2}\right)\log\left(w - \frac{1}{2}\right)$$

$$- \left[\left(l - \frac{1}{2}\right)\log\left(w_0 + \frac{1}{2}\right) - \left(l + \frac{1}{2}\right)\log\left(w_0 - \frac{1}{2}\right)\right] \tag{12}$$

and

$$y = x\left[\frac{1}{2} - R + w\left(1 - 8R + 4R^2\right)^{\frac{1}{2}}\right] \tag{13}$$

where the parameter l is given (as before) by Eq. (9) and w increases from its initial value w_0 at the beginning of the reaction, given by

$$w_0 = \left(R - \frac{1}{2}\right)\left(1 - 8R + 4R^2\right)^{-\frac{1}{2}},$$

to its final value of infinity.

The above equations were used for evaluating a series of corresponding numerical values for x, y, and u for various values of R. The results of these calculations are shown in Figures 1 and 2 where y is shown as a function of u for various values of R. When experimental values for y and u are available (as in the case of our investigation of the decomposition of sodium hypobromite solutions), y is plotted against u and the appropriate value of R is then found by comparing this experimental curve with the theoretical curves shown in Figures 1 and 2. These curves can be used equally well when x rather than u is the quantity determined experimentally, for, in such cases, u can be calculated from the experimental values of x and y by means of Eq. (5).

It is of interest to consider the behaviour of y towards the end of the reaction. (This problem has been discussed by several authors for the case of two primary reacting species[1,10,11]). Eq. (8), applicable when $R < (1 - \sqrt{3}/2)$, shows that the ratio y/x tends to a limiting value as the reaction approaches its end, i.e. as $x \to 0$ and $v \to \frac{1}{2}$. This ratio, which we denote by α, is given by

$$a = \frac{1}{2} - R - \frac{1}{2}\left(1 - 8R + 4R^2\right)^{\frac{1}{2}}.$$

It can be seen immediately from Eq. (5) that the ratio y/u tends to the limiting value $a/(1 + 2a)$ as $y/x \to a$. Hence, for these values of R, it follows that $y \to 0$ and $u \to 0$ as the reaction approaches its end; in other words, the chemical reaction goes to completion, the final products being C and D only. These points are brought out clearly in Figure 1.
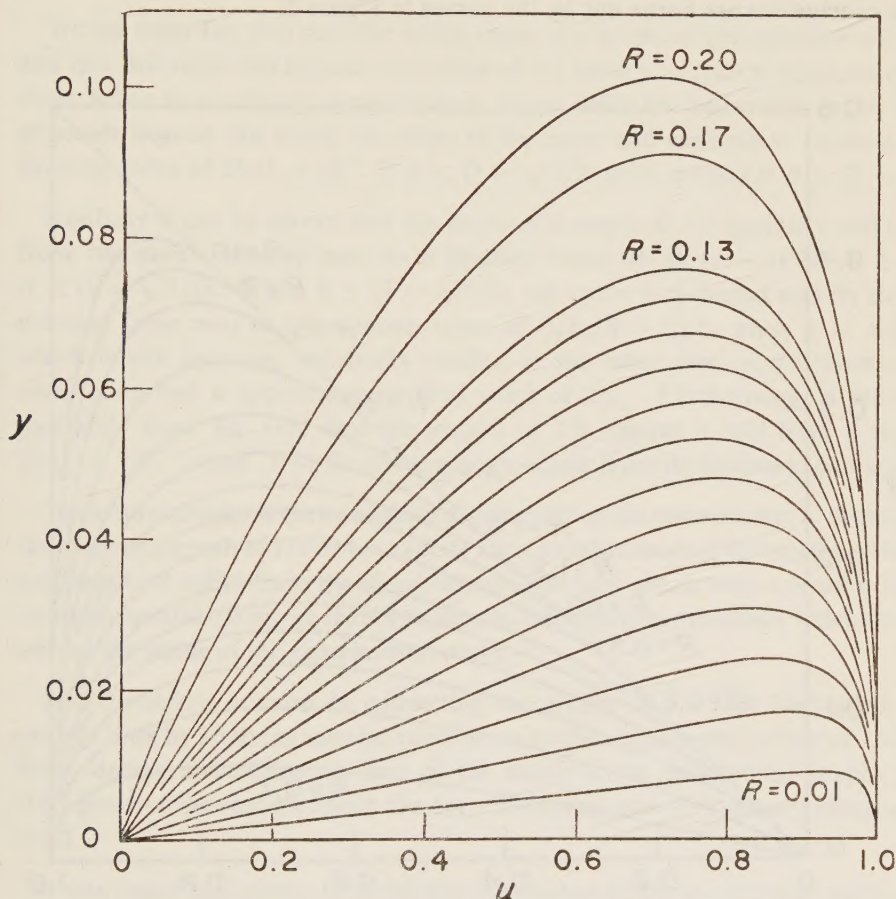
Figure 1

Curves showing y as a function of u for various values of R between 0.01 and 0.20. The curves between $R = 0.01$ and $R = 0.13$ correspond to increments of 0.01 in R.

On the other hand, if $R > (1 - \sqrt{3}/2)$, it can be shown that y tends to a finite limiting value as the reaction approaches its end. In other words, some of the intermediate B will remain at the end of the reaction together with C and D. We denote this limiting value of y by y_∞. If $R < (1 + \sqrt{3}/2)$, it follows from Eqs. (10) and (11) that y_∞ is given by

$$\log y_\infty = \frac{1}{2}\log R - m(\pi/2 - \theta_0),$$

while if $R > (1 + \sqrt{3}/2)$, Eqs. (12) and (13) lead to the relation

$$\log y_\infty = \frac{1}{2}\log(1 - 8R + 4R^2) + \left(l + \frac{1}{2}\right)\log\left(w_0 - \frac{1}{2}\right) - \left(l - \frac{1}{2}\right)\log\left(w_0 + \frac{1}{2}\right).$$

Furthermore, it follows from Eq. (5) that $u \to 2\,y_\infty$ as the reaction approaches its end. These conclusions are borne out by the curves in Figure 2.
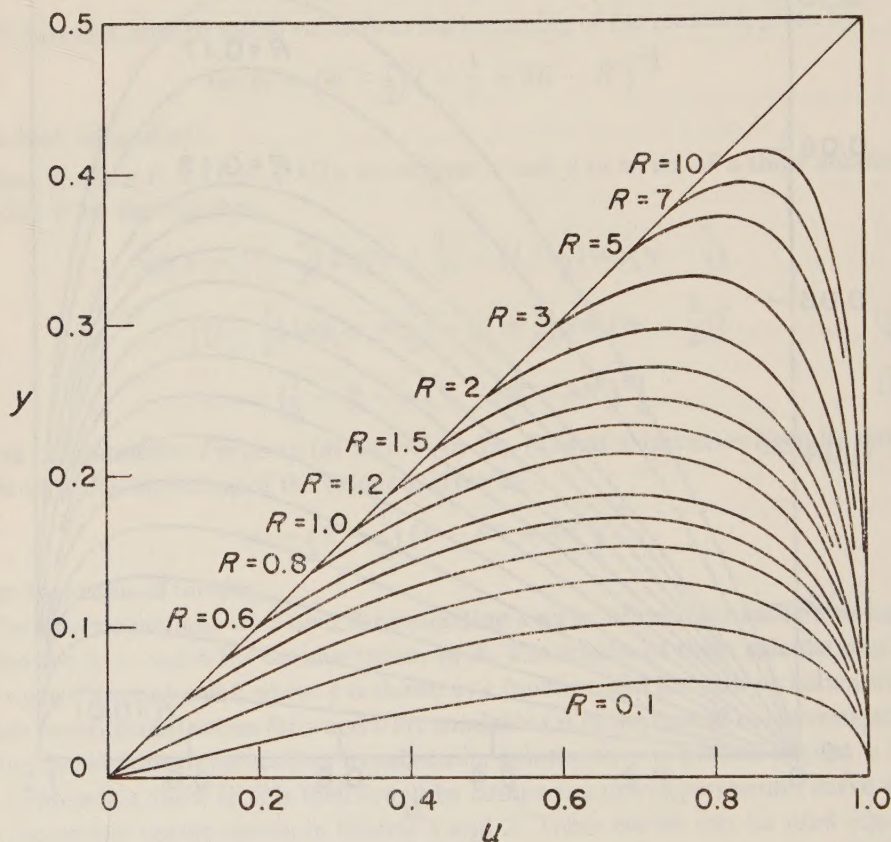
Figure 2

Curves showing y as a function of u for various values of R between 0.1 and 10.0. The curves between $R = 0.1$ and $R = 0.6$ correspond to increments of 0.1 in R.

DETERMINATION OF THE RATE CONSTANT k_1

We have already seen that when R is extremely small, the rate constant k_1 can readily be determined, since, under these circumstances, graphs of both $1/x$ and $1/u$ against τ will give straight lines having a slope equal to $3k_1$. However, in the more general case when R is no longer extremely small, these graphs will not be straight lines.

It follows from Eqs. (2), (3), and (5) that the slopes of these graphs at any point will be given by

and

$$d(1/x)/d\tau = k_1[2 + y/(Rx)] \tag{14}$$

$$d(1/u)/d\tau = 3k_1xy/(Ru^2). \tag{15}$$

We see from Eq. (14) that the initial slope of a graph of $1/x$ against τ will be $2k_1$ and that this slope will increase to a value of $3k_1$ when $y = Rx$, i.e. when the intermediate B has its maximum concentration. It can easily be shown that as the reaction proceeds beyond this point, the slope of the curve will continue to increase — to a limiting value of $3k_1(1 - \alpha)^{-1}$ if $R < (1 - \sqrt{3}/2)$ or to infinity if $R > (1 - \sqrt{3}/2)$.

Similarly it can be shown that the slope of a graph of $1/u$ against τ will increase from its initial value of zero to a limiting value of $3k_1(1 - \alpha)^{-1}(1 + 2\alpha)^{-1}$ if $R < (1 - \sqrt{3}/2)$. When $R > (1 - \sqrt{3}/2)$, the curve is S-shaped and its slope will increase from zero to a maximum value of $3/8\,k_1/R = 3/8\,k_2$ when $y = x/2$, after which it will decrease, eventually tending to the value zero as the reaction nears completion and u approaches its final value of $2\,y_\infty$. Furthermore, it follows immediately from Eq. (15) that the graphs of $1/u$ against τ will have a slope of $3k_1(1 + 2R)^{-2}$ when $y = Rx$ and the intermediate B has its maximum concentration.

These results suggest the possibility of determining the rate constant k_1 by measuring the slope of a graph of $1/x$ or $1/u$ against τ at a suitable stage of the reaction. However, such methods suffer from the disadvantage that they utilize only a small portion of the experimental curve; we therefore suggest the following procedure which effectively utilizes the whole of the experimental curve.

This procedure consists in converting the graphs of $1/x$ and $1/u$ against τ into straight lines by applying suitable corrections to the experimental values of $1/x$ or $1/u$. Since, during a considerable part of the reaction, the uncorrected graphs do not differ greatly from straight lines* the corrections required are in general comparatively small.

It was found convenient to define the corrections to $1/x$ so that their values would be zero when $1/x$ had the arbitrary values of 1.1 and 1.6. (The reasons for the choice of these particular arbitrary values are explained in the next section.) It follows that the corrected straight-line graph of $1/x$ against τ will coincide with the uncorrected

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* For small values of R such that $R < [19 - 3\,(33)^{\frac{1}{2}}]/16$, it can be shown that these curves tend towards asymptotic straight lines having slopes of $3\,k_1(1 - \alpha)^{-1}$ and $3k_1(1 - \alpha)^{-1}\,(1 + 2\alpha)^{-1}$ respectively. Moreover, for values of R appreciably smaller than this critical value, the curves of $1/x$ and $1/u$ against τ will almost coincide with these asymptotic straight lines, except during the early stages of the reaction.

curve at these two points. Similarly the corrections to $1/u$ were defined so that their values would be zero when $1/u$ had the same two arbitrary values.*

In order to obtain these corrections we first evaluated $k_1\tau$ at various stages of the reaction for a series of values of R ranging from 0.01 to 10.0. For values of R between 0.01 and 1.0 we obtained a suitable expression for $k_1\tau$ by combining Eqs. (2) and (3) to give

$$3k_1 d\tau = -(1/x^2)\,dx + (1/x^2)\,dy = d(1/x) - d(y/x^2) + (2/x)\,d(y/x)$$

which on integration gives

$$3k_1\tau = \left(\frac{1}{x} - \frac{y}{x^2} - 1\right) + 2\int_0^{y/x} \frac{d(y/x)}{x} \quad . \tag{16}$$

Eq. (16) can be transformed by means of Eqs. (8) and (11) into

$$3k_1\tau = \left(\frac{1}{x} - \frac{y}{x^2} - 1\right) - 2(1 - 8R + 4R^2)^{\frac{1}{2}} \int_{v_0}^{v} \frac{dv}{x} \tag{17}$$

and

$$3k_1\tau = \left(\frac{1}{x} - \frac{5}{x^2} - 1\right) + 2\left(-\frac{1}{4} + 2R - R^2\right)^{\frac{1}{2}} \int_{\theta_0}^{\theta} \frac{d\theta}{x \cos^2 \theta}, \tag{18}$$

respectively. Eq. (17) is applicable when $R < (1 - \sqrt{3}/2)$ whereas Eq. (18) is the corresponding equation when $(1 - \sqrt{3}/2) < R < (1 + \sqrt{3}/2)$. On the other hand, for values of R greater than unity, an alternative procedure was more convenient; Eq. (2) can be integrated to give

$$2k_1\tau = \left(\frac{1}{x} - 1\right) + \int_1^x \frac{y\,dx}{x^2(y + 2Rx)}$$

and can then be transformed by means of Eqs. (10) and (11) into

$$2k_1\tau = \left(\frac{1}{x} - 1\right) - \left(-\frac{1}{4} + 2R - R^2\right)^{-\frac{1}{2}} \int_{\theta_0}^{w} \frac{y\,d\theta}{x^2}, \tag{19}$$

and by means of Eqs. (12) and (13) into

$$2k_1\tau = \left(\frac{1}{x} - 1\right) - (1 - 8R + 4R^2)^{-\frac{1}{2}} \int_{w_0}^{w} \frac{y\,dw}{x^2(w^2 - \frac{1}{4})}, \tag{20}$$

respectively. Eq. (19) is the appropriate equation when $(1 - \sqrt{3}/2) < R < (1 + \sqrt{3}/2)$, while Eq. (20) applies when $R > (1 + \sqrt{3}/2)$.

P. 102, Eq. (18),

Instead of $\dfrac{5}{x^2}$, read $\dfrac{y}{x^2}$

Eq. (19).

Instead of $\displaystyle\int_{\theta_0}^{w}$, read $\displaystyle\int_{\theta_0}^{\theta}$

P. 103. line 21.

Read: ... include the two points for
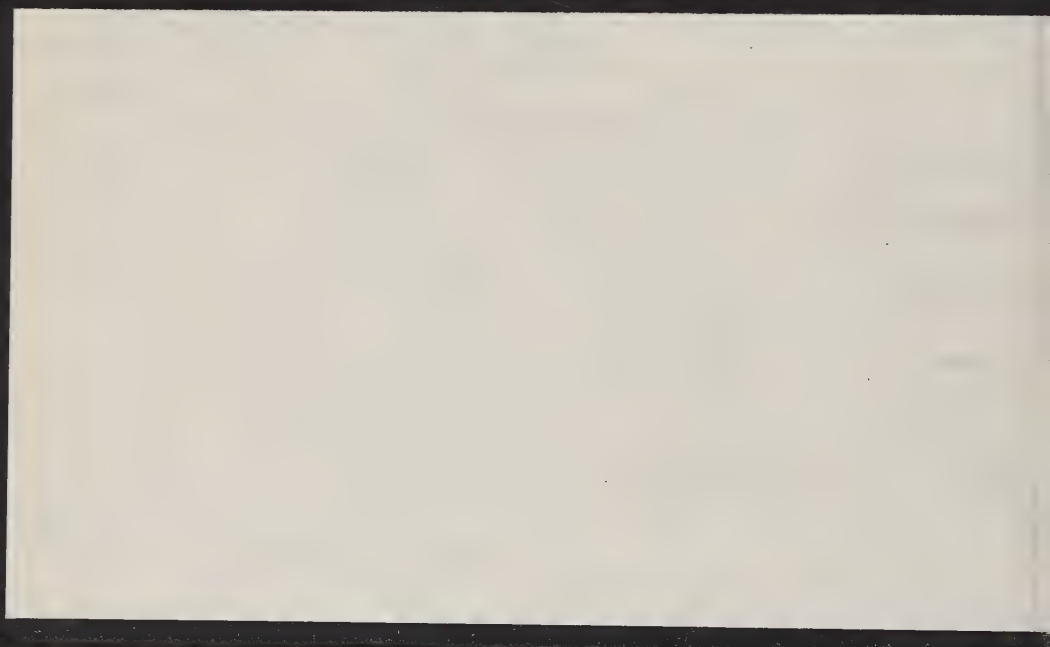
For each of the values of R considered, x, y, and u were evaluated for a series of round values of v, θ or w by means of Eqs. (5), (7), (8), (10), (11), (12), and (13). In addition, the corresponding values of $k_1\tau$ were evaluated by numerical integration of Eqs. (17), (18), (19), and (20) using Simpson's rule (When $R = 2$ the integral in Eq. (20) can readily be evaluated in closed form and numerical integration is unnecessary). The values of $k_1\tau$ corresponding to suitable round values of $1/x$ and $1/u$ were then obtained by graphical interpolation of these results. The corresponding corrections to $1/x$ were calculated from the formula

$$\frac{1.1(k_1\tau)_{1.6} - 1.6(k_1\tau)_{1.1} + 0.5(k_1\tau)_{1/x}}{(k_1\tau)_{1.6} - (k_1\tau)_{1.1}} - \frac{1}{x} \, ,$$

where $(k_1\tau)_{1/x}$ is the value of $k_1\tau$ corresponding to a particular value of $1/x$. The results obtained are shown in Figures 3 and 4, plotted against the corresponding values of R. The ratio of the slope of the corrected ($1/x$ against τ) curve to the rate constant k_1 is given by the factor $0.5/[(k_1\tau)_{1.6} - (k_1\tau)_{1.1}]$ and is shown by the broken curves in Figures 3 and 4, as a function of R. The corresponding results for the corrections to $1/u$ and the slopes of the corresponding corrected curves were calculated by similar formulae and the results are shown in Figures 5 and 6.

When the value of R is known, the curves given in Figures 3, 4, 5, and 6 are used in the following manner. The uncorrected experimental values of $1/x$ or $1/u$ are first plotted against τ and a smoothed curve is then drawn through the points. The appropriate corrections corresponding to the known value of R are then read off from Figure 3, 4, 5 or 6, as the case may be, and applied to this smoothed experimental curve to give a series of "corrected points" which of course include the points for which the corrections are zero ($1/x$ or $1/u$ equal to 1.1 and 1.6). If the reaction mechanism we are considering and the value of R used are both correct, these "corrected points" will lie on a straight line within the limits of experimental error. Finally, the value of k_1 is obtained by dividing the slope of the "best" straight line through the "corrected points" by the appropriate factor obtained from the broken curve in Figure 3, 4, 5 or 6, as the case may be.

DETERMINATION OF R AND k_1 WHEN CONCENTRATION OF INTERMEDIATE B IS NOT MEASURABLE

The above method can often be used for determining R and k_1 in cases when the concentration of the intermediate B cannot be measured, provided that the experimental data is of rather high accuracy. In essence the method consists of applying the appropriate corrections to $1/x$ or $1/u$, as the case may be, for various values of R and choosing that value of R for which the "corrected points" fall as nearly as possible on a straight line. The value of the rate constant k_1 is then obtained from the slope of this line, exactly as before.

Figure 3

The full curves show the correction to be added to $1/x$ as a function of R for low values of R. The broken curve shows the ratio of the slope of the corresponding corrected curve to the rate constant k_1.

In practice the labour involved in this process can be reduced considerably by first obtaining a rough estimate for the appropriate value of R. This is done by first drawing a straight line through the two points on the smoothed experimental curve for which the corrections are always zero ($1/x$ or $1/u$ equal to 1.1 and 1.6). The corrections which must be applied to the smoothed curve in order to convert it into

Figure 4

The full curves show the correction to be added to $1/x$ as a function of R for medium and high values of R. The broken curve shows the ratio of the slope of the corresponding corrected curve to the rate constant k_1.

this straight line are then noted for a series of suitable round values of $1/x$ or $1/u$. The range of values of R giving corrections of the required order of magnitude can then be determined from Figures 3 and 4 or from Figures 5 and 6. The "corrected points" for a series of values of R in this range are then plotted until they fall as nearly as possible on a straight line. It should be stressed that this straight line will, in general, not coincide exactly with the straight line drawn before; no special weight should be given to the points for which $1/x$ or $1/u$ has the values 1.1 and 1.6.

The choice of 1.1 and 1.6 as the values of $1/x$ and $1/u$ requiring no correction, was based on the following considerations: in order that the above rough estimate for the appropriate value of R shall be reasonably good, the straight line drawn through those two points on the smoothed experimental curve for which the corrections are always zero must coincide as far as possible with the "best" straight line through the "corrected points". It is clearly advisable that these two points should not be too close together and that they should be situated in regions in which accurate kinetic data are normally obtained. The value of 1.1 was thought preferable to that of 1.0 since, in practice, the first point on a kinetic curve is often less reliable than the remainder; furthermore, it was believed that a kinetic study of such a reaction would normally be continued long enough to include the value of 1.6 not only for $1/x$, but also for $1/u$, which, for large values of R, increases much more slowly than $1/x$.

It can be seen from Figure 3 that the absolute values of the corrections to $1/x$ pass through a maximum when $R \simeq 0.25$ and that the corrections corresponding to a value of R somewhat less than this (say 0.2) will not differ significantly from the corrections corresponding to a somewhat larger value of R (in this case 0.35). For this reason, if the progress of the reaction is followed by measuring x, the method of determining R just described cannot be used when R has a value in the neighbourhood of 0.25. For similar reasons, if the progress of the reaction is followed by measuring u, the above method cannot be used for determining values of R in the neighbourhood of 0.15, as can be seen from Figure 5.

The method described in this section is similar in principle to the time ratio method of Frost and Schwemer[6]. The connection between the two methods is easily seen since, in any given run, the time required for x to drop from unity to a particular value x will be proportional to

$$(\text{correction})_{1/x} \quad — \quad (\text{correction})_{1.0} + (1/x - 1)$$

where $(\text{correction})_{1/x}$ denotes our correction to $1/x$ for the appropriate value of R. However the time ratio method is not suitable for a competitive consecutive second order reaction involving only one primary reacting species since the time ratios would in many cases be only slightly dependent on the value of R, while R will not, in general, be a single-valued function of these time ratios. Furthermore, we believe the graphical method described in this section to be superior to the time ratio method in that it enables the experimental data over the whole range of the reaction to be surveyed at one time and shows up more clearly the above-mentioned limitations of these methods for certain ranges of values of R.
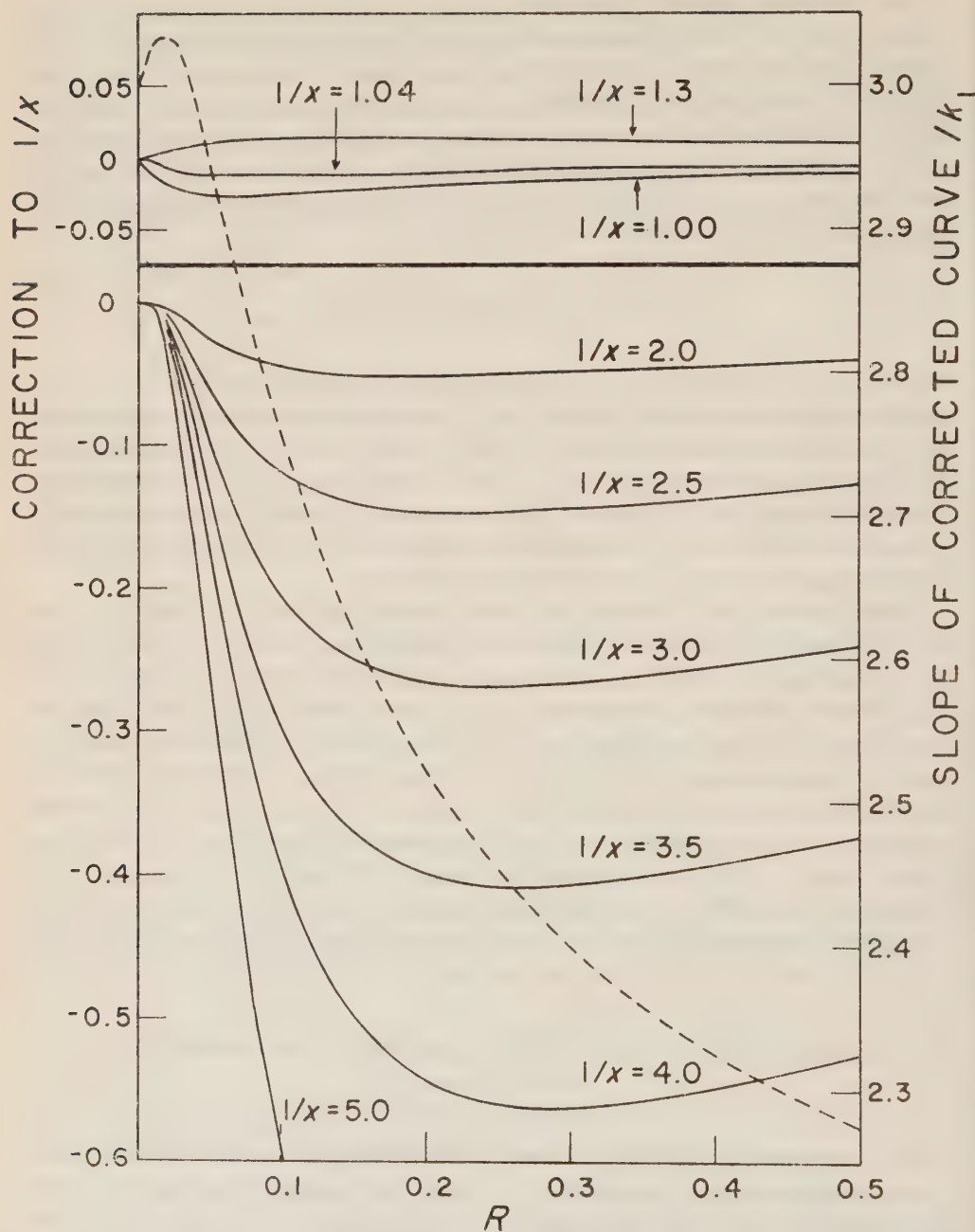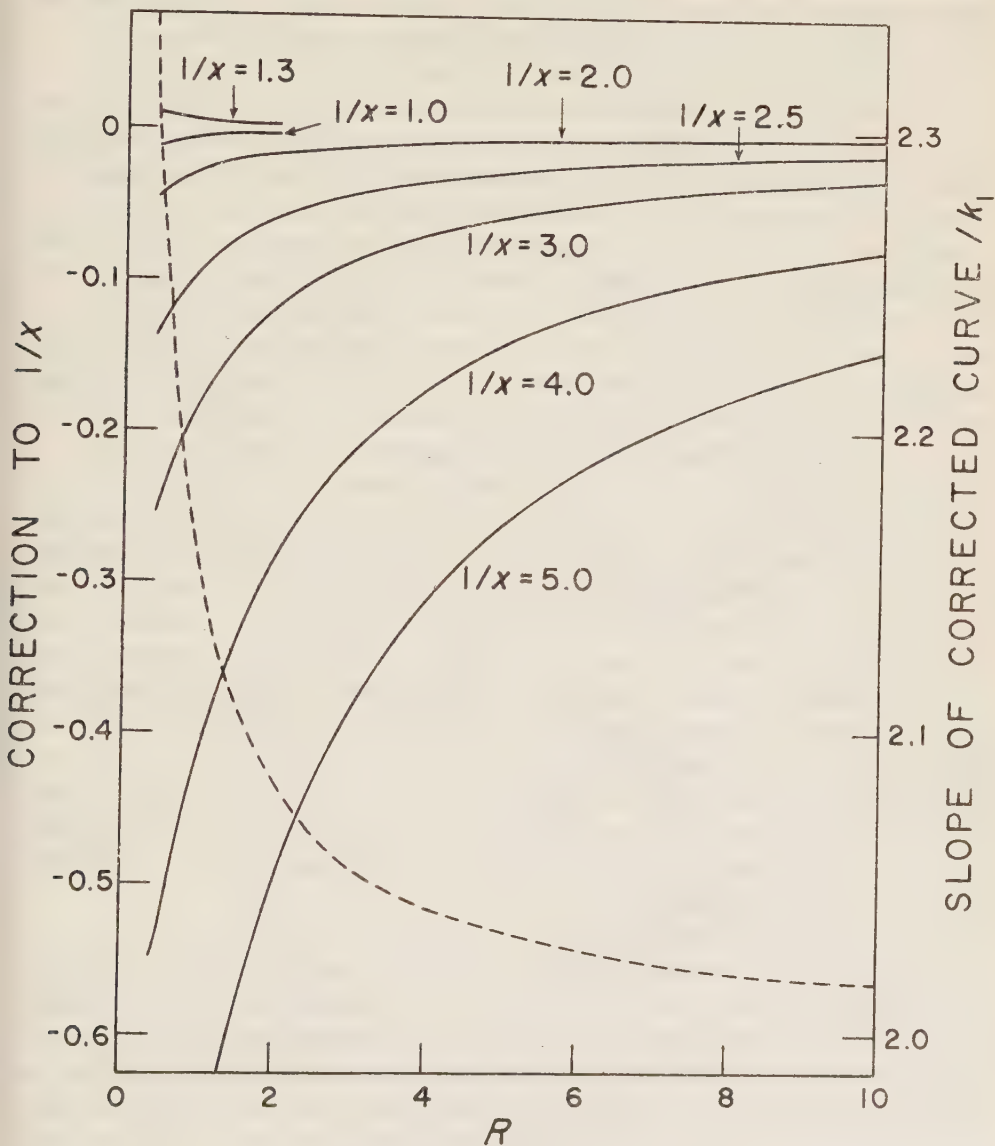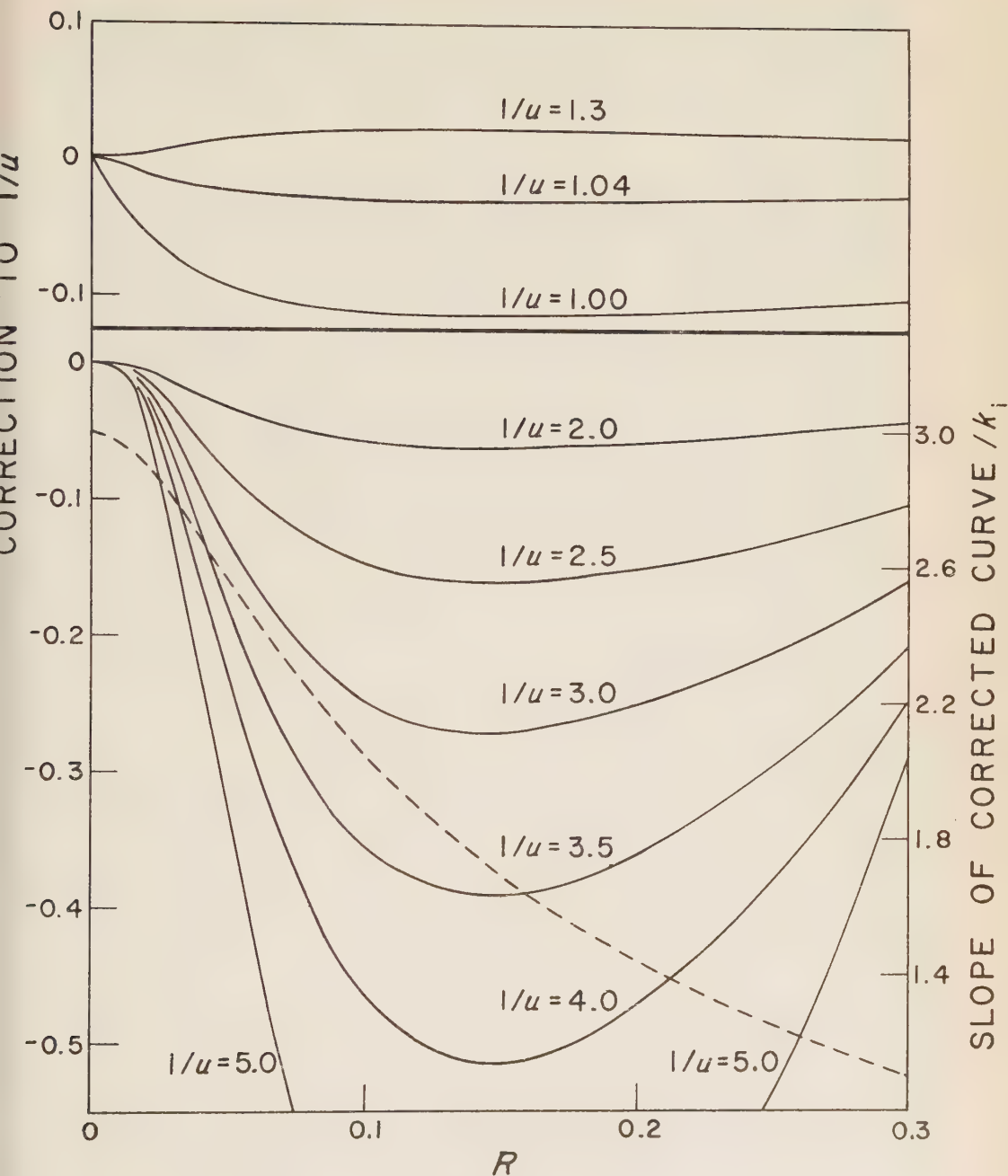
Figure 5
The full curves show the correction to be added to $1/u$ as a function of R for low values of R. The broken curve shows the ratio of the slope of the corresponding corrected curve to the rate constant k_1.

Finally, it must be stressed that, for certain values of R, graphs of $1/x$ or $1/u$ against time differ only imperceptibly from straight lines over an appreciable portion of the course of the reaction. For this reason, considerable reserve must be exercised in interpreting such experimental straight-line graphs, obtained over a limited
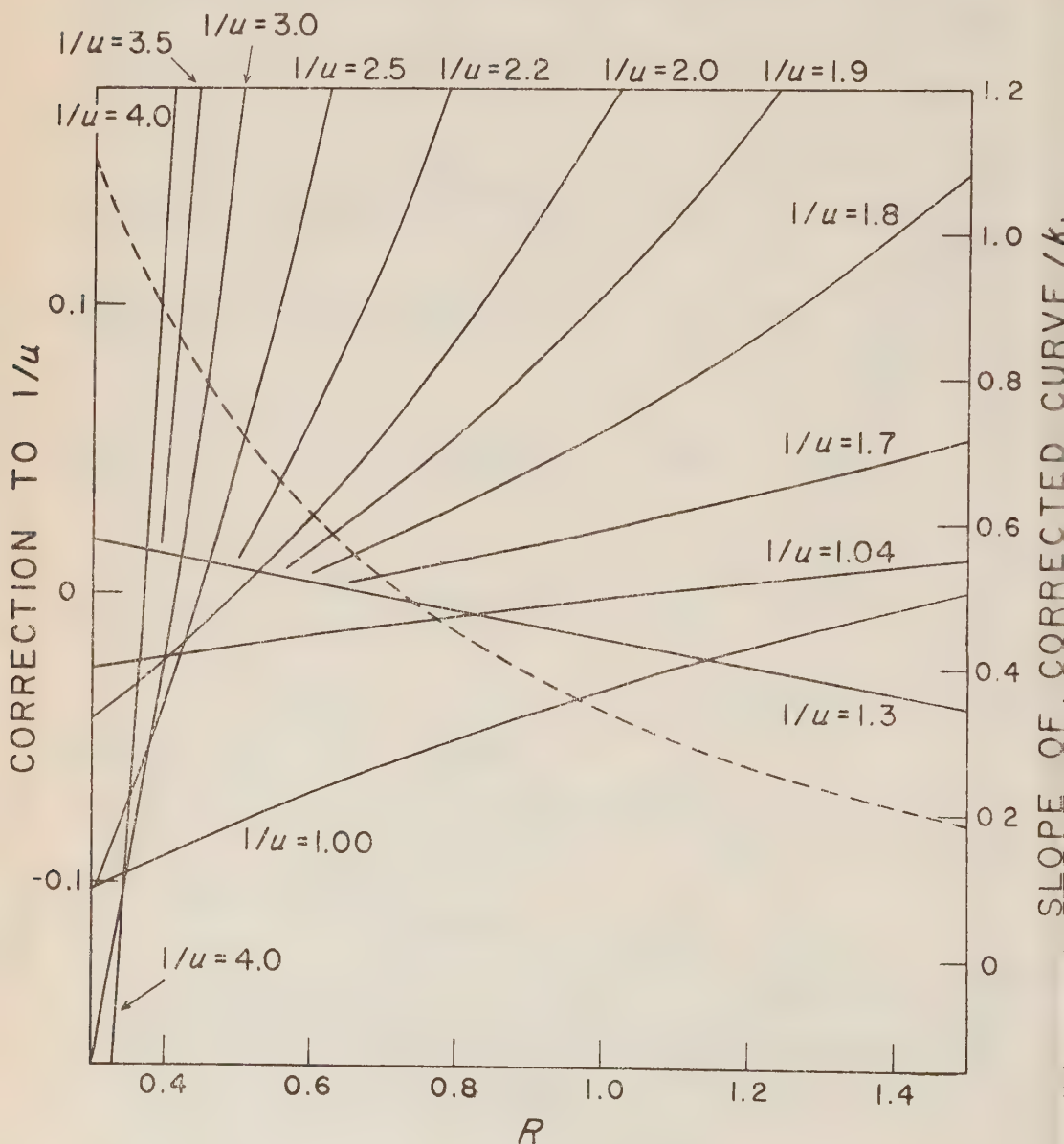
Figure 6

The full curves show the correction to be added to $1/u$ as a function of R for medium values of R. The broken curve shows the ratio of the slope of the corresponding corrected curve to the rate constant k_1.

portion of the course of the reaction, as proving the existence of a stationary concentration of the intermediate B. In fact we ourselves were led into such an error at one stage of our investigation by the fact that when $R \simeq 0.4$ the graph of $1/u$ against time is practically a straight line for values of $1/u$ between 1.1 and 3.0.

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THE STRUCTURE OF 3,4-DIHYDROXYAZOBENZENE-4'-SULPHONIC ACID

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ABSTRACT

The preparation of 3,4-dihydroxyazobenzene-4'-sulphonic acid from catechol and sulphanilic acid by two methods is described. The trans-configuration revealed by X-ray powder diffraction analysis and the strong hydrogen bonding found in infrared spectra are indicative of inter-molecular association.

3,4-Dihydroxyazobenzene-4'-sulphonic acid was examined in our laboratories as a selective reagent for potassium[1]. Its preparation by two methods yielded different looking products — bronze coloured plate-like crystals (Form A) and a yellow amorphous powder (Form B). However, both the infrared spectra and X-ray diffraction characteristics for the two forms were identical. The colour difference was most probably a result of different crystalline size or the presence of trace impurities.

The appearance of only strongly associated hydroxyl groups in the infrared spectra of the reagent indicated association of both the phenolic groups as well as the sulphonic acid group. Catechol did not show hydrogen bonding under the same conditions of analysis. A comparison of the X-ray diffraction data of the sulphonic acid with those of azobenzene indicated that the reagent exists in the trans-configuration. Hydrogen bonding must therefore be intermolecular.

Association of this type has been reported for *p*-hydroxyazobenzenes [2,3]. *o*-Hydroxyazobenzenes may associate intramolecularly[4,5] giving rise to stable cis-isomers[6]. In all the examples quoted in the literature, association was apparently between the phenolic and azo groups. Even catechol and azobenzene form a 1:1 molecular complex in solution[7].

<div align="center">

EXPERIMENTAL

Preparation of Form A
</div>

The 3,4-dihydroxyazobenzene-4'-sulphonic acid could not be prepared as described by Bevillard[1]. The method of Kuznetsov and Nemodruk[8] was employed. These authors' conclusions concurred with ours; the coupling of diazonium chlorides with catechol in alkaline solutions yielded only gas and tar and no coupling occurred in

acidic solutions. The phenolic groups were therefore complexed with aluminium prior to the introduction of the diazonium salt.

Sulphanilic acid hydrate (19.1 g (0.1 mole)) was mixed with 68 ml of water and 14 ml of concentrated hydrochloric acid. Then a solution of 7.0 g (0.1 mole) of sodium nitrite in 12.0 ml water was slowly added to the above mixture with stirring at 6–9°C. Each addition caused a temperature rise but no colour change occurred. The mixture was stirred an additional 10–15 minutes and then added at 5–10°C with stirring to 11.0 g (0.1 mole) of catechol and 37 g of $Al_2(SO_4)_3 \cdot 18H_2O$ dissolved in 100 ml of H_2O.

The resulting red mixture turned cocoa-brown in 10–15 minutes. At this point, 100 ml of a 20% aqueous sodium acetate solution was added over a 45 minute period. The red colour returned. Concentrated hydrochloric acid (30 ml) was added and the resulting red-brown mixture was permitted to warm to room temperature. At no time prior to this did the temperature rise above 10°C. The crude product was filtered with suction and recrystallized from hot water (solubility, approximately 1 g/l) using a Soxhlet extractor. This compound decomposed slowly upon heating without melting; nor did it melt when injected into a preheated block. It was insoluble in common organic liquids and its alkaline solution decomposed rapidly.

As reported[1] the reagent readily reacted with potassium chloride solutions to yield its potassium salt.

Anal.   Calcd. for $C_{12}H_9N_2O_5SK$:   C,43.3; H,2.7; N,8.4
            Found: C,42.9; H,2.8; N,9.1

Preparation of Form B

Concentrated hydrochloric acid, 3.0 ml, was added to a solution of 12.5 g (0.065 mole) of sulfanilic acid hydrate and 4.3 g of Na_2CO_3 in 43 ml of water. The mixture was stirred 15 minutes, cooled to 5–10°C, and then 5.1 g of sodium nitrite dissolved in 9.0 ml water was slowly added with stirring. A bright orange color developed. Stirring was continued 0.5 hour and then 8.0 g (0.072 mole) of catechol was added. The mixture became more fluid and lighter in colour. The resultant yellow paste was filtered and purified with water.

The properties of this product were similar to those reported for Form A and it produced the identical potassium salt in approximately the same yield. It was identified with Form A by comparison of the infrared spectra of the two products as well as those of the potassium salts and by the X-ray diffraction data.

Infrared and X-ray diffraction analyses

The infrared spectra (KBr phase) of the two forms were identical and revealed the expected peaks. Strong hydrogen bonding was indicated in both spectra by the broad OH absorption bands which appeared at 3130 cm^{-1}. The spectrum of catechol

under the same conditions revealed the unassociated 3330 cm^{-1} OH band. The following bands were observed in the 1000–3500 cm^{-1} region of the reagent spectra:

3130, 1620, **1598,** 1523, 1470, 1440, **1380, 1290, 1270, 1245, 1220, 1157, 1140, 1122, 1107, 1033, 1008.**

X-ray diffraction data were obtained by the Debye-Scherrer method using a copper target X-ray tube with a nickel filter (λ Cu = 1.54 Å); camera diameter, 5.73 cm (1 mm = $2°\theta$); voltage, 36 Kv; 20 mA; and an exposure time of 3 hours. Relative intensities were estimated visually. No difference was found between the patterns of forms A and B.

The identification of the compound with the trans- or cis-form of azobenzene was not carried out by direct experimental evaluation. However, the crystallographic data, interplanar spacings and relative intensities of the sulphonic acid agreed well with the data given in the ASTM diffraction data card[9] for unspecified "azobenzene" (see Table I). By comparison of the crystallographic data of the latter with that given by Wyckoff[10] (see Table II) the ASTM compound was shown to be the trans-isomer.

TABLE I

The comparison of crystallographic data of 3,4-dihydroxyazobenzene-4'-sulphonic acid (DSA) with ASTM diffraction card "azobenzene" standard[9]

ASTM "Azobenzene"				D S A	
d: 4.55 — 3.81 — 5.18				4.41 — 3.86 — 5.33	
I/I_0: 100 — 100 B — 60				100 B — 100 B — 10	
d	I/I_0			d	I/I_0
7.10	40			7.49	10
5.70	10			5.98	10
5.18	60			5.33	10
				4.76	100[a]
4.55	100			4.41	100[b]
4.22	20			4.11	100[c]
4.06	10			3.96	20
				3.86	100[a]
3.81	100 B				
3.66	30				
				3.54	100[b]
3.53	10				
3.33	20				
				3.29	100[c]
3.21	40				
3.11	40			3.11	40
3.03	40			2.93	100 ?
2.91					
				2.81	5–10
2.71	40				
				2.63	20
2.54					
				2.41	20
2.35	3				
2.29				2.29	30
2.19				2.17	10
2.11				2.11	20–30[a]
2.02	30			2.05	20–30[c]
1.99	10				
1.90	10 VB			1.89	15
1.80	40			1.83	15
1.81	10				
				1.77	20
1.76	10			1.73	15[b]
etc...				etc...	

a — Inner edge of line measured
b — Center of line measured
c — Outer edge of line measured

TABLE II

Comparison of crystallographic data of cis- and trans-azobenzenes

Crystallographic System		ASTM "Azobenzene"[9] Monoclinic	Trans-Azobenzene[10] Monoclinic	Cis-Azobenzene[10] Orthorhombic
Lattice parameters (Å)	$a_0 =$	12.65	12.20	7.57
	$b_0 =$	6.06	5.77	12.71
	$c_0 =$	15.6	15.40	10.30
Interaxial angles		$\beta = 114°24'$	$\beta = 114°24'$	

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    a — Trans-azobenzene XIV; I (16), Text a 11; fig. A 20-a-b.
    b — Cis-azobenzene XIV, I (16), Text b 4; fig. B 5-a-b.

LETTERS TO THE EDITOR

The action of trypsin on α-N-methyllysine ethyl ester, SHOSHANA AHLFELD, S. KUK-MEIRI AND N. LICHTENSTEIN, *Department of Biological Chemistry, The Hebrew University of Jerusalem*

N-Methyl and N-ethyl derivatives of phenylalanine ethyl ester were found to be resistant to the action of chymotrypsin[1] while this enzyme readily hydrolyzed the unsubstituted ester[2]. It is known that lysine ethyl ester is hydrolyzed by trypsin[3]. In view of the above findings, it appeared of interest to find out how the substitution of one hydrogen atom of the α-amino group of lysine ethyl ester by an alkyl group would affect its susceptibility to the action of trypsin.

DL-α-N-methyllysine ethyl ester dihydrochloride was prepared in the following way: Ten g of ε-benzoylamino-α-bromocaproic acid[4] were treated with 50 ml of aqueous methylamine (25 to 30 per cent w/v) at 28° for 3 days. The solution was evaporated *in vacuo* to dryness with repeated addition of alcohol. The residue was rubbed up with 100 ml of ethanol and allowed to stand for 24 hours. The precipitate formed was filtered and washed with alcohol until free of bromide ions. Yield, 7.2 g. Ten g of the crude ε-benzoylamino-α-N-methylamino caproic acid were boiled with 60 ml of concentrated hydrochloric acid and 40 ml of water for 10 hours. The solution was cooled and the benzoic acid was filtered off. The filtrate was evaporated *in vacuo*. The syrupy residue was dissolved in 80 ml of dry ethanol and the solution was saturated with dry hydrogen chloride. After evaporation *in vacuo* the esterification procedure was repeated. The reaction mixture was again evaporated *in vacuo* and the residue was dissolved in 40 ml of hot dry ethanol. To the filtered solution 120 ml of dry ether were added. The precipitate was recrystallized from 8 parts of hot dry ethanol. Yield, 5.7 g.

Anal. Calcd. for $C_9H_{22}O_2N_2Cl_2$: N, 10.7; Cl, 27.1; neutral equivalent, 131; Found: N, 10.5; Cl, 27.3; neutral equivalent (Willstätter-Waldschmidt-Leitz titration), 131.

DL-Lysine ethyl ester dihydrochloride was prepared by esterifying DL-lysine hydrochloride with ethanol-hydrogen chloride in the usual manner[3]. It was recrystallized from alcohol-ether.

Anal. Calcd. for $C_8H_{20}O_2N_2Cl_2$: Cl, 28.7; neutral equivalent, 124. Found: Cl, 28.9; neutral equivalent (Willstätter-Waldschmidt-Leitz titration), 122.

Worthington crystalline trypsin, 1x crystallized (50 per cent $MgSO_4$), was used. Its action was followed by measuring the disappearance of ester according to Hestrin's hydroxamic acid method[5].

The results summarized in Table I show that, contrary to the unsubstituted lysine ethyl ester, the N-methyl derivative was not affected by trypsin at a pH range varying between 5.6 and 7.8.

TABLE I

The action of trypsin on lysine ethyl ester and on α-N-methyllysine ethyl ester

Substrate	pH	Time (minutes)			pH	Time (minutes)		
		0	10	20		0	10	20
LEE*	5.6	285	252	240	6	285	220	195
LEE**	5.6	283	280	286	6	285	280	270
MLEE***	5.6	280	280	280	6	290	280	270
MLEE**	5.6	280	272	280	6	290	280	272
LEE*	7	290	210	150	7.8	290	220	170
LEE**	7	290	280	285	7.8	280	280	280
MLEE***	7	260	260	262	7.8	260	263	262
MLEE**	7	260	258	256	7.8	262	264	262

*   DL-Lysine ethyl ester dihydrochloride.

**   No enzyme added.

***   DL-α-N-Methyllysine ethyl ester dihydrochloride.

Each reaction mixture contained: phosphate buffer, 0.1M, 6 ml; substrate, approximately 60 μmoles; trypsin, 0.2 mg. Temperature, 30°. 1 ml samples were tested by Hestrin's method (10 min treatment with hydroxylamine prior to the addition of HCl and FeCl$_3$). The figures in the Table represent the Klett-Summerson colorimeter readings (Filter 54).

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Preparation of β-aspartohydroxamic acid, NATHAN DE GROOT AND N. LICHTENSTEIN, *Department of Biological Chemistry, The Hebrew University of Jerusalem*

β-Aspartohydroxamic acid has been used as a substrate in a number of enzymatic studies[1-6]. Using the method described for its preparation from asparagine[7], we obtained unsatisfactory results. We found, however, that L- and D- β-aspartohydroxamic acid can be conveniently obtained from L- or D-aspartic acid in the following way:

β-Methyl ester hydrochloride of L- and D-aspartic acid is prepared by treating the corresponding isomer of aspartic acid with dry methanol containing hydrogen chloride as described by Coleman[8]. The methanolic hydrogen chloride solution is easily obtained from methanol and acetyl chloride[9]. The reaction mixture is kept at room temperature for 24 hours and the ester hydrochloride is precipitated with dry ether. After standing overnight in the cold, the precipitate is filtered and washed with ether-methanol (3:1). The yield is about 15 g from 25 g of aspartic acid. The product so obtained gives, in the Sorensen formol titration, correct neutral equivalent values and is used as such in the following steps.

A solution of 6.6 g triethylamine (3 moles) in 25 ml of dry methanol is added to a cooled mixture of 4 g of L- or D-aspartic acid β-methyl ester hydrochloride (1 mole), 3 g of hydroxylamine hydrochloride (2 moles) and 60 ml of dry methanol. The mixture is kept at room temperature for 6 to 7 days. Eighty ml of dry methanol are added and the mixture is kept at room temperature for 3 additional days. The hygroscopic precipitate formed is filtered through a sintered glass funnel, washed with dry methanol and immediately dried in a vacuum dessicator over sulphuric acid. The product is dissolved in 10 volumes of water. To the filtered solution the double volume of dry ethanol is added. After a few hours, the precipitate is filtered and washed with ethanol-water (2:1). This product, which is not hygroscopic, is recrystallized by dissolving it in 20 volumes of water and precipitating with the double volume of dry ethanol. The precipitate is washed with ethanol-water (2:1) and recrystallized in the s me manner. Yield, 1.25 to 1.35 g. The products so obtained were found to be chromatographically pure but for traces of aspartic acid*. The specific rotation of L- β-aspartohydroxamic acid is $[\alpha]_D^{25} + 27.9°$ (2 per cent solution in N HCl). The corresponding value for the D-isomer is $[\alpha]_D^{25} - 27.7°$.

Anal. L-Isomer Calcd. for $C_4H_8O_4N_2$: C, 32.4; H, 5.4; N, 18.9. Found: C, 32.5; H, 5.4; N, 19.1. D-Isomer: Calcd.: N, 18.9; Found: N, 18.7.

* We are indebted to Dr. Y. S. Halpern, Department of Bacteriology, The Hebrew University-Hadassah Medical School, for carrying out the chromatographic tests.

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BOOK REVIEWS

NEUERE ANSCHAUUNGEN DER ORGANISCHEN CHEMIE, by EUGEN MUELLER, 2nd ed., XII + 550 pp. Springer-Verlag 1957, DM. — M. G. 59.60

This textbook of theoretical organic chemistry for advanced students by Professor E. Mueller, Director of the Laboratories of Applied Chemistry at Tuebingen University, is a rewritten version of his work, which first appeared in 1940. The material is divided according to bond-types, e.g., $C — H$, $C — C$, $C — Hal$, $C — O$, $C — N$ bonds, $C = C$ and $C = O$ double bonds, aromatic bond systems, etc. etc. The treatment of several phenomena rather suffers from this division. Thus, for instance, the discussion on resonance starts in the chapter on carbon-carbon double bonds (pp. 144–153), and is then taken up again on p. 317, with the treatment of aromatic bond systems. Again, the attempt to divide reactions accurately often leads to the omission to point out their similarities. Thus the common features of the pinacol and Hofmann rearrangements are not pointed out, as no mention is made of the generalisations of the Whitmore mechanism.

The author, in his foreword, writes that the presentation of reaction kinetics was omitted, as suitable monographs exist on the subject. Nevertheless, it is rather a pity that there is practically no discussion at all of kinetic proofs of reaction mechanisms. For the reader accustomed to English texts, some of the nomenclature is strange. Admittedly, the term "carbonium ion" may be incorrect, as it is not an "onium" compound. Still its use is accepted internationally and its substitution by "carbenium-ions" is hardly justified. Even less justified is the use of "carbeniat-anion" instead of the simple "carbanion".

Some minor errors were noted: The statement (p. 256), that the hydrogen atom in the carboxyl group belongs *equally* to both oxygen atoms, is not correct. The H_2^+-ion is called H_2^+-molecule (p. 5). The condensation product of a cyanohydrine and an aldehyde (in the acyloin-condensation, p. 218) is called a "dimeric" anion. The statement (p. 247) that the greater the ease of ionisation of a methylene-group, the greater will be its "reactivity", is misleading. The nitronium ion NO_2^+ is sometimes called nitronium-cation, and sometimes "nitryl-ion" (p. 372–3).

Aside from the above criticisms, this is a very readable and valuable text. The literature references generally include 1954 and even 1955. There is a wealth of references of historical interest, especially on the work of German chemists, some of which are rarely included in English books. The treatment of the material is clear and up-to-date. There are some excellent photographs of molecular models — one would like to see their use increased in other books on organic chemistry. The printing, paper and binding are very good.

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TEXTBOOK OF ORGANIC CHEMISTRY, by CARL R. NOLLER (Professor of Chemistry, Stanford University) Second Edition, 1958, 654 pages, W. B. Saunders Company, Philadelphia, London, $7.00

This is a concise companion book to Noller's comprehensive treatise, *Chemistry of Organic Compounds,* reviewed above. The general conception and the basic approach are essentially identical in both publications. In accordance with the advances made in organic chemistry since the appearance of the first edition of this book (1951), much of the old material has been revised and new added, e.g. conformation, inclusion compounds, ferrocene, tropolones, insulin and oxytoin, al-

dosterone and lanosterol, organic boron and aluminium compounds, and silicon derivatives with functional groups. Recent important technological applications have likewise led to additions, e.g that of polyisoprene and urethane rubbers, and of epoxy-and polyester resins and other subjects.

On the other hand, the discussion of advanced topics such as annular reactions, sigma complexes and natural acetylenic compounds, and theoretical discussions on such matters as nuclear and electron spin resonance, the use of molecular orbitals in dealing with covalent bonding and resonance, absorption spectroscopy and other subjects contained in the *Chemistry of Organic Compounds* are omitted in the book under review.

Considerations of the mechanism of organic reactions are again introduced at an early stage (Chapter 3) and used throughout the book. Even a random opening of the book reveals the up-to-date presentation; for instance, on page 372, where the various sulfonamides are structurally discussed, together with their use against anaerobic bacteria, such as anthrax, the hypoglycaemic effect of N-(*p*-tolylsulfonyl)-N$'$-(*n*-butyl) urea (orinase), recently so important in the oral treatment of diabetes, is also given, as is the use of *p*-aminophenyl-sulfone and its derivatives in the treatment of leprosy.

By judicious editing, the author has succeeded in keeping the number of pages comparatively low.

This book can be recommended to anybody who requires an up-to-date but not a too extensive treatment of organic chemistry. He will be helped in the assimilation of the material by the inclusion in the book of review questions and of problems at the end of each chapter.

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Jerusalem

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CURRENT TRENDS IN HETEROCYCLIC CHEMISTRY, Proceedings of a Symposium held at The John Curtin School of Medical Research, Australian National University, Canberra, Sept. 2–4, 1957, under the auspices of THE CHEMICAL SOCIETY; Organizer and Chairman: Professor ADRIEN ALBERT, D. SC., F.R.I.C.; Editors: A. ALBERT; G. M. BADGER, D. SC., F.R.I.C.; C. W. SHOPPEE, D. SC., F.R.I.C., F.R.S., Butterworths Scientific Publications, London, 1958, $ 5.50

This publication represents the proceedings of a symposium on the above subject held in Canberra, Australia, in September 1957. It contains twenty lectures delivered on this occasion on rather divergent subjects, the common denominator being the fact that they all belong to the vast field of heterocyclic chemistry. The topics include: Reactions of Ethyl Diazoacetate with Heterocyclic Systems (G. M. Badger and B. J. Christie); The Reaction of Benzoyl Peroxide with Heterocyclic Compounds (K. H. Pausacker); Factors Influencing Electrophilic Substitution in Nitrogen Heterocycles (R. D. Brown); Addition to Double-bonds in N-Heteroaromatic Six-Membered rings (A. Albert); Physico-Chemical Studies on Solubilized Porphyrins (J. N. Phillips); Stereochemistry of Catechins and Related Flavan Derivatives (J. W. Clark-Lewis); Quantitative Studies of Tautomerism in Heterocyclic Mercaptans (A. Albert and C. B. Barlin); The Effect of Heteroelements in Modifying some Cyclizations: Part I. Polycyclic Aromatic Compounds from the Diene Synthesis (W. Davies and Q. N. Porter); Part II. Benzofuran Derivatives Formed by Cyclization of ω-Aryloxyacetophenones (W. Davies and S. Middleton); The Possible Formation of Thiazoline and Thiazolidine Rings in Peptides and Proteins (J. M. Swan); The Linear Naphthiminazoles (D. J. Brown); Synthetic Routes to Mono-Substituted Phenanthridines (W.H.F. Sasse); A Novel Type of Naturally Occurring Quaternary Base (J. R. Price); Hernandine — A New Aporphine Alkaloid from *Hernandia bivalvis* Benth (R. Greenhalgh and F. N. Lanhey); Some Alkaloids of Australian Crotalaria species (C. C. J. Culvenor); Quinolizidine Alkaloids (W. D. Crow); Syntheses of Pyrimidine Nucleosides (G. Shaw); Spectrum and Bond-Type in Metalloporphyrins (J. E. Falk and R. S. Nyholm); Hydropteridines and their Biological Role (R. L. Blakley); Biotransformation Products of ^{14}C-Labelled Codeine and Morphine (T. K. Adler); The Reactivity of Some Pyridine Derivatives in Enzyme Systems (M. R. Atkinson).

A stimulating feature of the book is the inclusion in full of the discussions which followed each of the papers.

For those actively engaged in research or work on one of the subjects discussed or for those who may be interested in informing themselves on one of the branches of organic chemistry actively pursued in Australia at present, the book will be a valuable and handy source of information.

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CHEMISTRY OF ORGANIC COMPOUNDS, by CARL R. NOLLER (Professor of Chemistry, Stanford University) Second Edition, 1957 (Reprinted March, 1958), 978 pages, W. B. Saunders Co., Philadelphia, London, $9.00

The book is characterized by a modern and broad approach to its subject without unduly neglecting the classical structural viewpoint. Molecular orbital theory in its fundamentals is already set out in the first, introductory, chapter and use is thereafter made of it and of considerations of reaction mechanism throughout the book. Physical and physico-chemical methods for the elucidation of problems of organic chemistry are extensively covered; e.g. a special chapter deals with the application of infra-red and nuclear magnetic resonance absorption to the determination of structure and with absorption in the ultra-violet and visible regions. The descriptive viewpoint is nevertheless not disregarded and a solid amount of factual information, including also up-to-date industrial implications of organic chemistry, is incorporated in the book. Justification exists for the intentional omission by the author of detailed discussions of the chemistry of biological processes on account of the necessity to keep the size of the book in reasonable bounds. Excellent text-books exist on this special subject. On the other hand, the chemistry of natural organic products is covered, and for a book of this size and general conception, proteins, amino acids, carbohydrates, alkaloids, steroids, terpenes, etc., are adequately treated. This holds also for stereochemical and other theoretical considerations. Newer developments in the various fields are included, as for instance in organic metallics, organic phosphorus and organic silicon compounds, in polymers, etc. Pertinent review questions and problems are given at the end of each chapter.

This is a modern, well-balanced treatise which can be fully recommended to the student majoring in chemistry as a text and first reference book.

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PROCEEDINGS OF THE ISRAEL CHEMICAL SOCIETY
AT THE THIRD CONVENTION OF SCIENTIFIC SOCIETIES
OF THE
ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE IN ISRAEL
Held in Haifa, October 19—21, 1959

The Israel Chemical Society was founded nearly 30 years ago and set up as its principal object the advancement of pure and applied chemical science.

Its main activities are concerned with the organisation of meetings for the reading of original papers, special symposia surveying fields of specific interest to a part of its members, and the organisation through its branches of local lectures, visits to industrial establishments and similar activities.

There are some 800 members of the society in Israel with branches in Jerusalem, Tel-Aviv, Haifa, Rehovoth and Beer-Sheba.

The permanent address of the Israel Chemical Society is: 30, Yehuda Halevy Street, Tel-Aviv.

The Society also follows with interest the professional status of its members and is one of the constituent bodies in the Association of Professionals ("Igud Ha'akademaim") in Israel.

The macro- and microdetermination of tetrabromoethane as applied in its manufacture and in its use in mineral dressing

A. Alon, D. Ader*, B. Bernas and N. Levite, *Israel Mining Industries Laboratories, Haifa*

The use of tetrabromoethane (TBE) as a heavy liquid medium for the enrichment of minerals on an industrial scale has been developed by the laboratories of Israel Mining Industries.

Within this program of work it became essential to develop analytical methods for the determination of TBE in a wide range of concentrations in Dead Sea brine, treated minerals and hydrocarbon solvents.

Dehydrohalogenation[1] with 0.1 N alcoholic KOH or complete saponification with KOH-*n*BuOH is used for the conversion of the organic bromo-compound to bromide. This in turn is determined:

a) Argentometrically (in the absence of chlorides), in the range from 10 mg to 200 mg TBE per aliquot.

b) Iodometrically, after the selective oxidation of bromide to bromate by sodium hypochlorite for the range from 400γ–10 mg and above per aliquot.

c) Colorimetrically, after oxidation to bromate and the liberation of Br_2 by the addition of KBr. The liberated bromine is then converted with rosaniline to the tetrabromorosaniline dye. Transmittance is measured at 540 μm. The Br_2: rosaniline ratio is critical. The range of determination is from 0–20 γ TBE per aliquot.

REFERENCE

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A spectrophotometric determination of small amounts of butyl alcohol by the use of vanadium oxinate

M. Stiller, *Israel Atomic Energy Commission, P. O. Box 7056, Tel-Aviv*

Feigl[1] describes a spot test for the detection of small amounts of alcohols by the action of vanadium oxinate, a red complex being formed which is extracted by benzene.

In the present work, a quantitative method was developed from the above-mentioned spot test in order to determine butyl alcohol in the presence of a high concentration of acetate ions.

The reaction, according to Feigl[1], is as follows:

(V oxinate)   Red complex
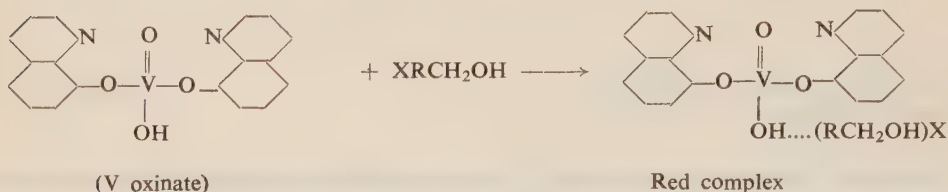
The complex of the vanadium oxinate with the butyl alcohol was examined spectrophotometrically. It had a convenient absorption band at $\lambda = 400 \, m\mu$.

Addition of sodium acetate was found to improve the extraction of the alcohol complex. The excess of vanadium oxinate (grey colour) was eliminated from the organic phase by extraction with an aqueous alkaline solution, while the red alcohol complex remains in the organic phase.

The method may be used to determine quantities as small as 5 ppm of butyl alcohol.

REFERENCE

FEIGL, F., 1956, "*Spot Tests in Organic Analysis*", Elsevier Publishing Company, p. 172.

A simple electrophoresis apparatus for the separation of serum proteins, lipids and hemoglobins

F. RAPPAPORT AND M. RABINOVITZ, *Bacteriology Laboratory, Hadassah Hospital, Tel-Aviv*

We present a simple electrophoresis apparatus for the separation of serum proteins, lipids and hemoglobins. This apparatus is assembled from easily available materials at low cost and provides excellent separation of the various components.

We present also our paper-agar method for clear-cut separation of A and F hemoglobin types, based upon their differential solubility in pH 5.6 — 5.8 buffer and movement in agar medium.

Second Session, Tuesday morning 20.10.59   Chairman: K. S. SPIEGLER
General Chemistry

Reactions between complicated organic and inorganic compounds on the boundary of the solid-solution state. A heterometric study

M. BOBTELSKY, *The Hebrew University of Jerusalem*

Chemical reactions between complicated compounds usually proceed only through the formation of intermediates. In each case the sequence, composition and character of the intermediates obtained depend on which of the reacting compounds is in

excess and which is present in only small quantities in the reacting system. Thus, a reaction between two such partners represents two series of intermediates revealing the points at which two reacting components attract each other. Of very great importance are the "*primary*" and the "*final*" compounds obtained. These are generally constituted otherwise than the compounds known from orthodox chemistry.

Heterometry presents, a unique and excellent method of studying complicated reactions proceeding through intermediates. Examples are given showing the importance of the results obtained in organic, inorganic, biochemistry and analytical chemistry.

Studies of reactions between alkaloids, proteins, thiocompounds, lakes and large inorganic ions

M. BOBTELSKY, M. COHEN, B. CARMON, I. BARZILAI AND J. GABAI, *The Hebrew University of Jerusalem*

The composition and structure of the compounds obtained in reactions between complicated organic molecules and inorganic complexes were studied .The structural formulas of the compounds are presented.

The organic compounds included are: Strychnine, quinine, cinchonine, sparteine, papaverine, atropine, antipyrine, rivanol, acroflavine, nitron, phenantroline, egg albumin and gelatine. The inorganic complexes participating in the reactions are: Noble metals, halogeno-complexes, iodine-iodide and bismuth iodide complexes, heteropolyacids such as phosphortungstic, phosphormolybdic and silicotungstic acids, tetraphenylboron, tetraphenylarsine, tetraphenyl phosphorus, etc.

The effect of alcoholic groups in amino-complexing agents upon the structure and properties of their copper complexes

B. KIRSON, *The Hebrew University of Jerusalem*

The alcoholic groups in amino-complexing agents tend to stabilize the copper complexes against hydrolysis. This effect is strengthened by an increase in the number of alcoholic groups in the complexing agent, and it was observed even in cases where they do not themselves participate in the co-ordination of the complexes.

This influence of the alcoholic groups exists equally if (1) these groups substitute the hydrogen atom of the amino group, as for instance in NH_2-ROH, $NH-(ROH)_2$ and $N-(ROH)_3$, or if (2) the alcoholic groups do not change the state of the nitrogen, as in compounds such as: $NH_2-R'OH$, $NH_2-R''(OH)_2$ and $NH_2-R'''(OH)_3$.

On the other hand, if the alcoholic groups of the amino-complexing agents are themselves active in coordinating the copper, results vary according as to whether the alcoholic groups are of type (1) or (2).

The kinetics and mechanism of the decomposition of *o*-nitrobenzazides in solution and in the solid state

Y. GOTSHAL* AND S. PATAI, *The Hebrew University of Jerusalem*

The thermal decomposition of *o*-nitrobenzazides gives, with the elimination of one molecule of nitrogen, the corresponding benzofuroxan derivatives[1]. We investigated the kinetics of this reaction in various solvents and in the solid state, both by a spectrophotometric method and by measuring the amount of nitrogen evolved.

It was found that the solvent had only a very slight influence on the rates, even though the solvents were of such widely differing dielectric constants as benzene, ethanol, dimethylformamide and formamide. As the reaction itself is most probably an ionic one (benzoyl peroxide has no effect), we believe that the results show that the mechanism is a strictly *intra*-molecular one, practically uninfluenced by the solvent.

In the solid state, sigmoid decomposition curves were obtained, and the maximum rates, after the inhibition period, were of the same order of magnitude as the rates in solvents.

TABLE I

Solvent	$10^5 \times k_1(\text{sec}^{-1})$	
	40°	48°
Benzene	1.3	3.3
Ethanol	1.8	4.2
Dimethylformamide	2.0	4.9
Formamide	2.1	—
Solid state (maximum)	~2	~8

REFERENCE
1. FAGLEY, T. F., SUTTER, J. R. AND OGLUKIAN, R. L., 1956, *J. Amer. chem. Soc.*, **78**, 5567.

Heterogeneous oxidation in the solid phase of polymers by $KClO_4$ in the presence of various ambient gases

M. ALBECK* AND S. PATAI, *The Hebrew University of Jerusalem*

The heterogeneous oxidation of a high-melting solid copolymer of divinylbenzene with ethylstyrene by solid $KClO_4$ has been investigated.

The mixture of the polymer with $KClO_4$ was pressed into tablets and heated at various temperatures. The percentage of reaction was determined by titrating the amount of chloride ions formed by the decomposition of the $KClO_4$. This was proportional to the temperature and the duration of the reaction. Considerable differences were found when the tablets were heated in closed ampoulles containing various gases; moreover the percentage of reaction, other things being equal, was

inversely proportional to the volume of the ampoules. The table gives results for tablets containing 71 % $KClO_4$ and 29 % of the polymer, heated for 20 hours at 400 °C.

| Initial pressure (mm Hg) | Gas | Volume of ampoulle | |
		30 cc Percent of reaction	15 cc Percent of reaction
700	O_2	56	65–69
0.02	Air	53	—
3	Air	50–52	63–67
700	Air	50	60
700	CO_2	42	56–60
700	N_2	33–36	49

The influence of the ambient gases depends probably on their absorption on the surface of the reactants. Compared to vacuum (i.e. 0.02 mm/Hg of air) all gases except oxygen retard the reaction. It is known from previous investigations[1,2] that $KClO_4$ is a catalyst for the oxidation of carbon by oxygen, and the same may be true for the oxidation of the polymer. If so, it can be assumed that the polymer is first partly oxidized by the oxygen and the product of this reaction oxidized faster by $KClO_4$ than the original polymer. The inhibition by gases which cannot react with the polymer is probably due to absorption on the reactant sufaces.

In some cases the kinetics of the heterogeneous oxidation have also been determined.

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2. PATAI, S., RAJBENBACH, L. AND HOFFMAN, E., 1952, *J. applied Chem.*, 2, 306, 311.

Influence of additives and pre-heating on the thermal decomposition of ammonium perchlorate

A. MAKOVKY AND A. SALMON, *Ministry of Defence and Technion–Israel Institute of Technology, Haifa*

The extent of thermal decomposition of mixtures containing ammonium perchlorate was determined in a vacuum apparatus, the pressure being measured as a function of time.

The results obtained satisfy the two equations:

$$\log \frac{p}{p_f - p} = kt + c \tag{1}$$

where p is the pressure at the time t and p_f the final pressure (Prout-Tompkins equation),

and

$$1 - (1-a)^{\frac{1}{3}} = kt \tag{2}$$

where α is the degree of decomposition at the time t.

As these two equations were developed by entirely different theoretical treatments of the process of solid-state decomposition, the agreement must be considered as fortuitous.

For all the measurements, the energies of activation and the pre-exponential factors obtained using the two equations, are in good agreement.

It has also been found that preheating of the perchlorate influences the rate of decomposition. All the catalysts used influence the decomposition of non-preheated perchlorate differently, whilst the decomposition curves of preheated perchlorate practically coincide for the different catalysts.

The thermal decomposition of nitroethane under high pressure

A. HERMONI-MAKOVKY AND T. B. GRUENWALD, *Technion–Israel Institute of Technology, Haifa*

The thermal decomposition of nitroethane has been studied under approximately 38 atmospheres pressure and over the temperature range 250–280 °C and shown to be approximately first order, with a rate constant given by

$$k = 10^{13,15} \, e^{-42200/RT} \, \text{sec}^{-1}.$$

The main products are water, nitric oxide, ethylene, carbon monoxide, methane, formaldehyde, nitrogen dioxide, hydrogen cyanide, carbon dioxide, and ethane. In addition to these, a solid residue accumulated as the reaction proceeded.

The rupture of the C-N bond as an initial step postulated for nitromethane is not applicable to the case of nitroethane because of the low activation energy obtained for the reaction.

The distribution of products obtained and the results of the kinetic investigation, which showed the entropy factor to be –1.6 cal. deg^{-1} mole^{-1}, suggest that under these conditions the decomposition of nitroethane proceeds by a unimolecular mechanism through cyclic activated complexes.

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1. MAKAVKY, A. AND GRUENWALD, T. B., 1958, *Bull. Res. Counc. of Israel*, 7A, 218.
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Fourth Session, Tuesday morning 20.10.59   Chairman: A. ALON
Analytical Chemistry

The characterisation of the tannin of the Israel *Eucalyptus rostrata* and methods of its analytical determination

E. KRAKAUER, J. FRANKL* AND M. LEWIN, *Institute for Fibres and Forest Products Research, Jerusalem*

In modern tannery practice it is essential to know to which group a given vegetable-tanning material belongs. Results of qualitative tests show that the tannin from

Eucalyptus rostrata bark is a mixture belonging in part to the catechol and in part to the pyrogallol type.

The tannin was examined according to the chromatographic procedure of Haddaway[1] which serves for the identification of individual vegetable-tanning materials.

The empirical hide powder quantitative tannin determination as adopted by the ALCA and AFCIC did not give reproducible results with *Eucalyptus rostrata* tannin, so that certain modifications had to be introduced. The concentration of the analytical solution had to be decreased and the analytical hide powder subjected to preliminary treatment before satisfactory results were obtained.

The possibility of applying for *E. rostrata* bark tannin the rapid spectrophotometric method of Roux[2] suggested originally for wattle tannin was investigated. Modifications in this method, consisting of adjustments of the wavelength region, the slit width of the Beckman D.U. spectrophotometer used and changes in the concentration of Thompson's grey standardisation solution, were introduced.

The amount of tannin which combines with collagen and the irreversibly combined fraction are important properties from a technical standpoint. Both were investigated.

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1. HADDAWAY, L. W., 1956, *Anal. Chem.*, **28**, 1624.
2. ROUX, D.G., 1955, *Wattle Tannin and Mimosa Extract*, Ed. Leather Industries Research Inst., Grahamstown, S. Africa, 153.

The determination of carboxyl groups in cellulose and oxycellulose

M. LEWIN AND J. A. EPSTEIN, *Institute for Fibres and Forest Products Research, Ministry of Commerce and Industry, Jerusalem*

Methods for the determination of carboxyl groups in cellulose are based on the cation exchange capacity of these groups. In the available methods, estimation may depend on cation exchange with calcium, sodium, silver or methylene blue. In all the methods, the cellulose is brought into contact with a solution of a salt containing the cation to be exchanged. Analysis may be based either on the estimation of the anion liberated, or the cation left in solution. In some cases the cation which has reacted with the cellulose is estimated directly.

In the present study nine different methods were examined using two samples of purified cotton, a sample of purified and bleached cotton linters and two samples of oxycellulose prepared by oxidation of the cotton linters with alkaline hypobromite. The relative merits of the different methods are discussed in the light of the results obtained.

## Determination of benzyl ester and carbobenzoxy groups

A. PATCHORNIK* AND S. EHRLICH ROGOZINSKI, *Department of Biophysics, The Weizmann Institute of Science, Rehovoth*

The benzyloxy group in esters, ethers, urethans and benzyl alcohol can be quantitatively converted into benzyl bromide by treatment with hydrogen bromide in acetic acid:

$$C_6H_5CH_2OCOR + HBr \rightarrow C_6H_5CH_2Br + RCOOH$$

The quantitative estimation of the benzyl bromide formed[1] is the basis of the determination of benzyloxy groups reported here.

Semimicro samples of various benzyloxy compounds were cleaved in 0.3 ml of 30% HBr in acetic acid[2]. After dilution with a known volume of benzene the mixture was extracted with an excess of 3 N aqueous alkali. Aliquots of the benzene layer were heated under reflux with an equal volume of aniline in the apparatus shown in Figure 1[3]. When the benzene had collected in B and the boiling point of aniline had been reached, the benzene was returned to the boiling flask A through stopcock F and this procedure repeated twice. The anilinium bromide formed[1]

$$C_6H_5CH_2Br + C_6H_5NH_2 \rightarrow C_6H_5CH_2NHC_6H_5.HBr$$
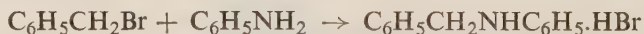
was then titrated directly with 0.02 N sodium methoxide using thymol blue as indicator.

With a considerable number of analytically pure carbobenzoxy amino acids and amino acid benzyl esters, titration values ranging from 97% to 100% of the theoretical were obtained.

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2. BEN ISHAI, D. AND BERGER A. 1952, *J. Org. Chem.*, **17**, 1564.
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B—
F—
A—
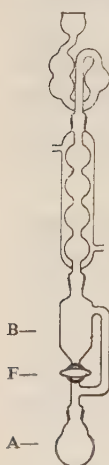
Figure 1

Fifth Session, Tuesday morning 20.10.59   Chairman: Y. MARCUS
Analytical Chemistry

A new method for the determination of O^{18} in phosphate ion

M. ANBAR, M. HALMANN and B. SILVER*, *The Weizmann Institute of Science, Rehovoth*

A method has been developed for the determination of O^{18} in orthophosphate based on the separation of the phosphate as trisilver phosphate which is subsequently decomposed by heat. The only gaseous product is oxygen gas, which may be analyzed directly in the mass spectrometer.

In the absence of interfering salts, phosphate ion is precipitated by the addition of a silver perchlorate solution adjusted to pH 5.8–6.2, centrifuged off, washed with water and dried in a vacuum oven at 60–70°. The precipitate is transferred to a platinum crucible and suspended by a platinum wire in a Pyrex vessel, which is evacuated to

less than 0.5 micron. The sample is heated in an induction furnace to 1000°. At this temperature silver phosphate decomposes; about 1 ml of oxygen gas at STP is obtained from 100 mg of trisilver phosphate. In a sample of phosphoric acid prepared by hydrolyzing phosphorus trichloride in H_2O^{18} (12.95 atom %), the oxygen obtained by pyrolysis of trisilver phosphate contained 12.68 atom % O^{18}. The probable error of the results was $\pm 2\%$.

This method is faster and less susceptible to errors of isotopic dilution than the method of equilibration of potassium dihydrogen phosphate with carbon dioxide[1], or pyrolysis with mercuric cyanide to yield carbon dioxide[2].

This investigation was supported in part by research grant RG 5842 from the Division of Research Grants, U.S. Public Health Service.

REFERENCES

1. COHN, 1949, *J. biol. Chem.*, **180**, 771.
2. WILLIAM AND HAGER, 1958, *Science*, **128**, 1434.

Preparation of hydrogen gas from inorganic and organic compounds for isotopic assay

M. ANBAR AND S. GUTTMANN*, *The Weizmann Institute of Science, Rehovoth*

The mercuric chloride method for production of carbon dioxide from oxygen-containing compounds, which was applied for isotopic oxygen estimation[1,2], produces hydrogen chloride as a by-product from hydrogen-containing compounds. The hydrogen chloride formed may be reduced with zinc amalgam at 200 °C to yield pure hydrogen.

This procedure was adopted for preparation of hydrogen from various compounds for the isotopic assay of hydrogen.

The method gives reproducible results both for deuterium and tritium in inorganic, aliphatic and aromatic compounds.

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1. RITTENBERG, D. AND PONTICORVO, L., 1956, *J. appl. Radiation and Isotopes*, **1**, 208.
2. ANBAR M. AND GUTTMANN, S., 1959, *J. appl. Radiation and Isotopes*, **5**, 233.

Determination of the isotopic composition of lithium and boron by the (n,α) reaction

J. LEONZINI*, *Ministry of Defence*, AND M. KANTER AND M. ANBAR, *The Weizmann Institute of Science, Rehovoth*

A method was developed to enable the assay of B^{10} and Li^6. The emission of alpha particles by the (n,α) reaction of boron-10 and the yield of alphas and tritons from the (n,α) reaction of lithium-6 was applied for determination of the isotopic composition of boron and lithium samples. In former experiments, lithium samples of "infinite" thickness were analyzed with an ionization chamber[1] or with a scintillation counter[2]. Lithium fluoride and potassium fluoborate samples of several isotopic ratios at thicknesses of less than 0.7 mg/cm^2 (finite thickness) were tested by us, utilizing a

multianode proportional counter. A method was worked out to prepare reproducible homogenous samples of lithium fluoride and potassium fluoborate of the necessary thickness. One to five mg LiF or KBF_4 were required per sample. These samples were subsequently assayed for their isotopic composition. A linear correlation between measured activity and the isotopic concentrations of Li^6 and B^{10} was found over a range of isotope concentrations from 7–96% Li^6 and 3–99% B^{10}. With a flux of approximately 3.10^3 n/cm^2 sec (Po-Be neutron source of 5 Curies surrounded by paraffin), the determinations of the isotopic composition were reproducible to $\pm$ 3%, in spite of the obvious handicaps of the preparation of such thin samples.

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Sixth Session, Tuesday morning 20.10.59   Chairman: A. GARBATSKY
Physical Chemistry

Ionic and solvent effects on the absorption spectra of ions in solution

GABRIEL STEIN AND AVNER TREININ[*], *Department of Physical Chemistry, The Hebrew University of Jerusalem*

In previous papers[1,2] a theory of the absorption spectra of anions, e.g. I^-, in solution was developed. The effect of temperature changes on the spectra were there compared with the theory. In the present work the theory is tested in the light of the changes caused in the spectrum by the addition of various salts and by changes in the solvent. The results enable one to derive information regarding the structure of aqueous ionic solutions and the effect of different ions on this structure, as well as regarding ionic radii in different solvents.

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The spectrum of I^- in aqueous solution below 2000 Å

JOSHUA JORTNER, GABRIEL STEIN AND BARUCH ZARETZKY[*], *Department of Physical Chemistry, The Hebrew University of Jerusalem*

In previous work[1] a theory of the absorption spectra of anions in aqueous solution was derived and tested by comparing its predictions with the effects of changes in temperature on the spectra. There, the spectrum of I^- was investigated down to 2000 Å. In the present paper the technique used to extend the range to 1860 Å is described. The effect of temperature on the energy band of I^- was investigated. The results are in agreement with the theoretical predictions.

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Absorption spectra of mercury (II), antimony (III) and bismuth (III) in pressed alkali-halide disks

A. GLASNER AND R. REISFELD*, *Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem*

In a previous work[1] measurements of the absorption spectra of thallium chloride and lead chloride in polycrystalline potassium chloride were reported.

Later[2] we proposed the use of these characteristic spectra in the evaluation of the diffusion constants of foreign cations in alkali halides.

In this work the spectra of bismuth chloride, antimony chloride, mercury chloride and mercury bromide in the alkali halides: potassium chloride, potasium bromide and sodium chloride were investigated. In every case the full developement of the characteristic absorption band was observed immediately after mixing of the two salts, and heating the mixtures did not increase the absorption.

The absorption bands are identical, or very nearly so, in the chlorides, and do not depend on the nature of the alkali cation, but the halide causes a shift in the absorption bands (the spectra are very similiar in all cases).

Experiments with various concentrations of mercury chloride in potassium bromide showed the Beer-Lambert law to be valid, which makes analytical determinations of mercury possible without dissolving the sample.

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The infrared spectra of salts containing a high concentration of O^{18}

S. PINCHAS* AND M. HALMANN, *The Weizmann Institute of Science, Rehovoth*

Silver nitrite of over 60 atom % O^{18} and potassium nitrate of 84 atom % O^{18} were examined as mulls in Nujol in comparison with the normal salts. The labelled silver nitrite showed absorption bands in the infrared region at 1365 (shoulder), 1227 (strong and broad), 847, 827 and 807 cm^{-1}. The two first bands seem to belong respectively to the ν_1 and ν_3 normal vibrations of the labelled nitrite ion. The last triplet must be assigned to branches of the ν_2 deformation vibration, which is split in the salt crystal under the effect of the lattice forces.

The labelled potassium nitrate absorbed at about 2010, 1755 (weak), 1073 (weak), 1028 (very weak), 969 (weak) and 817 cm^{-1}. As a mull in decalin the substance also showed a band at 705 cm^{-1}. The 1028 cm^{-1} band probably corresponds to the ν_1 frequency of the free nitrate ion, that of 817 cm^{-1} to the ν_2 and the 705 cm^{-1} band to its ν_4 vibration. The absorptions at 1755 and 969 cm^{-1} seem to be the result of the ν_3 splitting because of lattice forces.

If the isotopic frequencies are calculated while neglecting these forces, very good agreement is obtained in the case of the v_3 frequency of silver nitrite and the v_2 band of potassium nitrate, but big discrepancies are met in the other cases.

Seventh Session, Tuesday afternoon 20.10.59   Chairman: M. BOBTELSKY
General and Inorganic Chemistry

The distribution of hydrochloric and hydrobromic acids between water and tri-*n*-butylphosphate

A. S. KERTES, *The Hebrew University of Jerusalem*

Tri-*n*-butylphosphate (TBP), a polar and highly basic non-electrolyte, is a useful solvent in liquid-liquid extraction processes. The nature of TBP solutions containing nitric acid and many other nitrates was studied in connection with the separation processes involved in radiochemistry.

Equilibrium conditions were measured for the distribution of hydrochloric and hydrobromic acids between water and TBP and for the water in the TBP. The swelling of the organic phase, its density, viscosity and the conductivity of the solute were measured, and from these experimental data the solute-solvent interactions between these acids and the TBP were formulated. Two well-defined species were found to exist: the first being $[TBP]_2$ HX and the second, analogous to those with nitric acid, being TBP. HX.

The extraction of heptavalent rhenium from aqueous nitric acid solutions by tri-*n*-butylphosphate

A. S. KERTES AND A. BECK*, *The Hebrew University of Jerusalem*

The extraction of lanthanide and actinide nitrates from aqueous solutions containing nitric acid into tri-*n*-butylphosphate (TBP) has largely been studied in connection with the separation processes of fertile and fissile materials in radiochemistry. Only qualitative results based on our previous partition chromatographic experiments are available with regard to the extractability of metals in a state of high valency, such as heptavalent rhenium.

As the first step towards our ultimate objective of the separation of permanganate, pertechnetate and perrhenate by the technique of liquid–liquid extraction, we investigated the nature of the TBP solutions containing water, nitric acid and perrhenate at various concentrations.

The initial aqueous concentration of the perrhenate in our experiments varied from 5×10^{-5} to 1×10^{-2} M, that of nitric acid from 0.1 to 16 M, and that of TBP in an inert diluent from zero to one hundred percent. In these experiments the

equilibrium solutions were fully analysed and the spectrum, conductivity, viscosity, density and swelling of the TBP phases were measured.

This fairly detailed study under a large variety of conditions enabled us to formulate the composition of the extracted species and to calculate the apparent equilibrium constants of the reactions involved.

Equilibrium studies in the system KCl-HCl-n-BuOH-H_2O

R. BLUMBERG, P. LEWI AND P. MELZER*, *Israel Mining Industries Laboratories, Haifa*

As part of a general programme of work on the use of partially miscible organic solvent in the preparation of inorganic compounds, the equilibrium system KCl–HCl–n-BuOH–H_2O was examined at 30°C in those regions where two liquid phases coexist. The individual distributions of KCl, HCl and H_2O between the two phases and the mutual effects were determined over a wide range of concentrations.

The presence of KCl in the system favours the transfer of HCl to the alcoholic phase; this effect is particularly marked at lower concentrations of HCl in the aqueous phase; at high concentrations of HCl the effect of KCl disappears.

As regards the water transfer, it was found that at a given concentration of HCl in the aqueous layer, less H_2O will be transferred to the alcoholic layer, the higher the KCl concentration.

At constant KCl concentration, an increase in the HCl content causes an increase in the transfer of H_2O to the alcoholic layer.

Ion-exchange study of triphosphate complexes

C. HEITNER-WIRGUIN, *The Hebrew University of Jerusalem*

The complexes of triphosphate were studied by the ion-exchange method in the absence and in the presence of other anions participating in the formation of the complex. The subject of study was anion exchangers with various degrees of cross-linking, in order to check the possibility of separation of the different existing complexes according to their size. This study made possible the determination of the composition and charge of the complexes and may be further used for the separation of the complexes.

Activity coefficients in anion exchange resins having various capacities and cross-linking

D. PARITZKY* AND Y. MARCUS, *Israel Atomic Energy Commission, Laboratories*

As one step in an attempt to understand the selectivity of anion exchange resins for metallic complexes, the effect of resin-dependant factors on the distribution of electrolytes between the resin and solution was studied.

The solutions contained alkali metal chloride at various concentrations and the resins were of the trimethyl-benzyl-ammonium type, cross-linked to a number of different percentages of DVB (divinylbenzene) having various capacities.

The solutions were equilibrated with known amounts of resin, the phases separated and chloride ion determined in both. From the data, activity coefficients in the resin phase were determined from the Donnan equilibrium expression:

$$m_c m_a \gamma \pm^2 = {_r}m_c \; {_r}m_a \; {_r}\gamma \pm^2$$

where r denotes resin phase, m molality and $\gamma \pm$ activity coefficients.

Since the m's were measured and $\gamma \pm$ known from the literature, it was possible to calculate ${_r}\gamma \pm$.

A correction function ${_r}F_a$ allowing the correlation of metal complex distribution data for various chloride solutions and resins was calculated from:

$$_r F_a = \log {_r}m_a \; {_r}\gamma \pm - \log ({_r}m_a \; {_r}\gamma \pm) \cdot m_a \gamma \pm = 1$$

This determination allows the separation of factors influencing the selectivity due to the resin and solution phases[1].

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Eighth Session, Tuesday afternoon 20.10.59   Chairman: A. GLASNER
Physical Chemistry

Copolymerisation of styrene with some of its derivatives containing nitrogen in the side-chain

M. KREISEL*, U. GARBATSKI AND D. H. KOHN, *Division of Chemistry, Technion–Israel Institute of Technology, Haifa*

Styrene was copolymerised with the following five of its derivatives: PhCH=CHCN (I), PhCH=CH(CN)$_2$ (II), PhCH=C(CN)COOC$_2$H$_5$ (III), PhCH=CHNO$_2$ (IV), and PhC(CN)=CH$_2$ (V). Polymerisations were carried out in bulk at 80°C, up to low conversions, and using Bz$_2$O$_2$ as initiator. After isolation, the composition of the products was calculated from their nitrogen content.

Runs with different monomer ratios were made to calculate the monomer reactivity ratios (r_1, r_2), according to the usual kinetic scheme of copolymerisation[1]. One series only, styrene with (V), obeyed this scheme. Monomer (IV) acted as a weak inhibitor of styrene.

Runs with (I), (II), and (III) enlarge on some work already reported by Borrows

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et al.[2] In these three cases, the effect of the penultimate unit in the growing polymer radical could be ascertained. Barb[3] explains this effect in terms of dipole-dipole repulsion between identical units. The effect requires a kinetic scheme with twice the number of reactivity ratios[4]; the experimental results fit this scheme. Existing data on this effect are summarised and a single parameter for its characterisation is proposed.

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The influence of solvent composition (ethanol-water) on an essentially unimolecular[1] reaction

JACOB ZABICKY* AND SAUL PATAI, *Department of Organic Chemistry "A", The Hebrew University of Jerusalem*

The rates of the condensation of ethyl cyanoacetate with anisaldehyde, benzaldehyde and p-nitrobenzaldehyde, were measured in solvents of compositions varying from pure water to 73.5% (w/w) ethanol. In the three cases studied, the reaction rate constants changed as a function of the solvent composition, the dependence being nearly linear in both branches of a curve with a maximum at 20–30% ethanol.

The results are explained by considering various effects interfering with each other, namely, the dielectric constant and the basicity of the solvents, both of which, alone, increase the rate of reaction by accelerating the ionisation

$$NC\text{–}CH_2\text{–}CO_2Et \longrightarrow NC\text{–}CH^{\ominus}\text{–}CO_2Et + H^{\oplus}$$
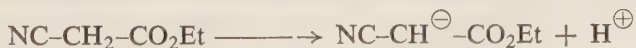
but at the same time, when adding ethanol to water, the dielectric constant decreases, while the basicity of the solvent increases. The results at low ethanol concentrations can also be interpreted by changes in the highly hydrogen-bonded structure of pure water, which is destroyed by the addition of ethanol[2,3].

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The acid-catalyzed racemization of adrenaline and related compounds

IDDO LEVIN* AND SHALOM SAREL, *Department of Pharmaceutical Chemistry, School of Pharmacy, The Hebrew University of Jerusalem*

The present communication is concerned with the elucidation of the mechanism of racemization of some physiologically active aryl ethanolamines catalyzed by mineral

acids. We have measured the first-order rate-coefficients for racemization of adrenaline, synephrine and related compounds in strong acid solutions at different temperatures. This study was aimed at establishing whether the rates of the reactions are proportional to Hammett's acidity function, h_o, or to the stoichiometric concentration of catalyzing acid. When the logarithms of the rates of racemization of adrenaline are plotted against values of Hammett's acidity function in its logarithmic form, H_o, a straight line of unit slope is obtained. From the observed H_o correlation it seems safe to conclude that the racemization of adrenaline goes through a "unimolecular" S_N1 mechanism. These results were also correlated with oxygen-exchange studies in O^{18}-labelled water. The effects of substitution in the aromatic nucleus upon both the course and mechanism of the reaction will be discussed.

The interaction of chloramine with nucleophilic reagents

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Different suggestions have been made as to the polarization of the N-Cl bond in chloramine NH_2Cl and its derivatives[1,2]. This polarization has been investigated by us, studying the interaction of chloramine and its derivatives with various reagents in aqueous solution, including iodide, bromide, chloride, hypochlorite, hydroxide, sulfite, hydrogen peroxide and arsenite.

The interaction with iodide and sulfite is very fast in weak and strong alkaline solutions. Bromide, nitrite and H_2O_2, on the other hand, interact very slowly with chloramine and methylchloramine in the pH range 8–14. The interaction with chloride ion was investigated by following the isotopic exchange between chloramine (and methylchloramine) with chloride. Chlorine-36 was used as tracer. This exchange was found to proceed, if at all, very slowly, upper limit $k < 10^{-5}$ l/mole/sec if first order in both reagents or $k < 10^{-9}$ sec if first order in one reagent and zero in the other.

This result suggests that chloramine has very little tendency to polarize according to $R\bar{N}H\text{-}Cl^+$. In this respect chloramine is different from its oxy-analog $HOCl$[3].

The interaction of chloramine with hydroxyl showed some evidence of attack on the nitrogen (and of forming an hydroxyl amine derivative), in addition to an attack on the chlorine, forming hypochlorite.

The kinetics of the interaction methylchloramine-arsenite were followed in the pH range 8–14 ($T = 30.6°$) and the following expression was found (in $l^2/mole^2$ min):

$$R = 8.8 \times 10^{10}(CH_3NHCl)(As^{III})\,(H^+) + 8 \times 10^2(CH_3NHCl)(As^{III})(OH^-).$$

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Ninth Session, Tuesday afternoon 20.10.59

Meeting of the Organisation Committee of the Israel Chemical Society

Tenth Session, Wednesday morning 21.10.59   Chairman: BAR-EL
Analytical Chemistry

Rapid paper-chromatographic determination of beryllium. A semiquantitative method applicable to geochemical investigations

A. ALON AND D. ADER*, *Israel Mining Industries Laboratories, Haifa*

Existing methods for the microdetermination of Be are lengthy and tedious. Owing to the high toxicity of beryllium an effort has been made to minimize manipulation.

A paper-chromatographic method has been developed. The interference of ions possessing an R_f similar to that of Be is eliminated by impregnating the paper with a 5% aqueous solution of EDTA. Development is effected with methylethylketone-HCl–H_2O or ethyl alcohol–HCl–H_2O. The chromatogram is sprayed with either morin or eriochrome-cyanine R solution and exposed to vapours of ammonia. Comparison is then made against standards for morin using ultraviolet light. Limits of determination: 0.002–0.5γ Be.

For rock samples a suitable aliquot is decomposed with HF–H_2SO_4 to remove silica. The residue is taken up with concentrated HCl and brought to volume with water. An aliquot of this solution corresponding to the above range is then applied. Less than 1 ppm in a sample can be detected.

a)   **Microdetermination of thorium by paper chromatography**

b)   **Application of paper chromatography for the fluorimetric microdetermination of uranium**

D. ELROI* (Th); A. ALON, D. BET HALAHMI AND D. ELROI* (U), *Israel Mining Industries Laboratories, Haifa*

A short discussion on the use of Whatman CRL/1 chromatographic paper (specially slotted sheets) in rapid semiquantitative inorganic analysis is presented. Details are given of a fluorimetric modification based on the method of Hunt, North and Wells for the determination of uranium. In addition a new method for the determination of Th (and U) is discussed, based upon the use of mesityl oxide as the developing agent. A description of the combined use of these approaches for the determination of low concentrations of U and Th in ores follows:

The ore is completely decomposed by variations of standard procedure. In certain cases a rapid solvent extraction with ethyl acetate is then performed on the solution (after addition of aluminium nitrate salting-out solution). Aliquots of the ethyl

acetate extract are evaporated in the presence of aluminium nitrate solution and the final concentrates are chromatographed, using mesityl oxide as solvent. Thorium is determined against standards (on parallel strips of paper on the same sheet as the unknown) after spraying with thoron. Uranium is determined by visual fluorimetry after ignition of the appropriate portion of the chromatogram followed by fusion with sodium fluoride-sodium carbonate flux.

The lower limit of determination of U is of the order of 0.02 ppm, and of Th 1 ppm, corresponding to 0.01γ U and 0.5γ Th.

To illustrate the accuracy of the method two samples (U.S. Bureau of Standards) were analysed.

The analyses reported on the certificates were:

		Th (ppm)	U (ppm)
Sample	1	10	0.4
Sample	2	100	4
Our results were:			
Sample	1	10	0.7–1.0
Sample	2	70	5–6

A method for the determination of small quantities of thorium in low-grade ores

J. YOFE AND S. YESSELSOHN, *Israel Atomic Energy Commission, P. O. Box* 7056, *Tel-Aviv*

The chemical analysis of thorium in silicate ores involves many difficulties, i.e. those of dissolving the sample and of determining the extremely small quantities of thorium in solution.

While typical thorium-containing ores such as thorianite or monazite contain thorium in an easily soluble form, in ordinary rocks such as granite, thorium is only a trace element and is mostly insoluble. Thus it can only be determined by dissolving the whole sample. Concentration of thorium from such ores in the final solution is less than a few tenths of a microgram per millilitre.

Thenoyl trifluoracetone, $C_4H_3S.CO.CH_2.COCF_3$ (TTA), solution in benzene was found to be a good selective solvent, and Morin (5,7,2′4 -flavanol)[1] a very sensitive colorimetric reagent for thorium—more sensitive, although less selective, than Thorin 1 (o-arsonophenoylazo-2-naphthol-3,6-disulphonic acid).

By shaking the sample solution (pH-1) with a TTA solution in benzene, only the thorium and uranium are extracted.

All the uranium is extracted from the organic phase by shaking with nitric acid (0.1 M), and the thorium is left in the organic phase.

The thorium is then extracted with 2 M HNO_3 and determined in the aqueous

solution by measuring the transmission of the thorium Morin complex, utilising a Beckman D. U. spectrophotometer at $\lambda = 410$ mμ and comparing the readings with a standard calibration curve.

As little as 0.2μg per ml of thorium in the tested solution could be determined, which corresponds to 5 ppm of thorium in the tested sample.

No interference due to the presence of Fe, Al, Mg, Ca, U, PO_4, SO_4 or Cl was found.

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Eleventh Session, Wednesday morning 21.10.59   Chairman: F. BERGMANN
Physical Chemistry

The isotopic exchange of iodine between *o*-iodo anisole and elementary iodine

M. ANBAR AND R. REIN*, *The Weizmann Institute of Science, Rehovoth*

The isotopic exchange of iodine between *o*-iodoanisole and elementary iodine in *n*-butanol has been investigated. The rate of exchange was found to be first order in *o*-iodoanisole and zero order in iodine. The rate constant found was $8.8 \pm 2.6 \times 10^{-8}$ sec^{-1} at 100 °C. The same exchange was followed in *n*-decane as solvent, and using the same rate expression it was found to proceed at a rate at least one-hundredfold slower.

Comparing these results with the *o*-iodoanisole iodide exchange, we find the same rate expression with a rate constant of $1.1 \pm 0.2 \times 10^{-8}$ at 100 °C. This rate was found to be slowed down by chloride ions and bases. A mechanism explaining these experimental results is presented.

The elucidation of the mechanism of acid hydrolysis of nitroparaffins using tracers

MICHAEL ANBAR AND DAVID SAMUEL*, *The Weizmann Institute of Science, Rehovoth*

A. The hydrolysis of nitroparaffins in concentrated sulphuric acid solutions to a carboxylic acid and hydroxylamine has been investigated with tracers.

$$R \cdot CH_2 \cdot NO_2 \xrightarrow{\text{H}_2\text{SO}_4 - \text{H}_2\text{O}} R \cdot COOH + H_2NOH$$
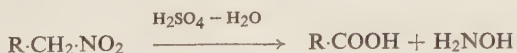
Using oxygen-18 labelled sulphuric acid and unlabelled nitromethane or 1-nitro-butane, hydroxylamine of normal isotopic composition was obtained. The carbon monoxide from nitromethane and the propionic acid from nitrobutane were found to contain oxygen-18. The former reaction was further investigated using carbon-13 labelled carbon monoxide. A hydration-dehydration mechanism is proposed for this reaction.

B. The mechanism was also examined of the Nef reaction, in which the salt of a nitroparaffin is hydrolysed by dilute acid to an aldehyde (or ketone) and nitrous oxide:

$$[RCH = NO_2] \longrightarrow RCHO + N_2O$$

On using oxygen-18 labelled solvents, the nitrous oxide formed was found to be of normal isotopic composition, whereas the aldehyde contained oxygen-18. A mechanism for this reaction is also proposed.

C. The exchange of oxygen between nitroparaffins and water in acid and basic solution has also been investigated.

The kinetics of the oxidation of D-glucose by bromine and by hypobromous acid

B. Perlmutter-Hayman* and A. Persky, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

The oxidation of glucose by bromine water has formed the subject of two previous investigations[1,2]. In the first[1], it was concluded from the dependence of the reaction rate on bromide concentration that *molecular bromine* is the oxidizing agent, whereas in the second[2], which considered the dependence on pH, *hypobromous acid* was concluded to be the active agent.

We repeated and extended these measurements and confirmed the experimental findings of *both* groups of investigators. The question of the oxidizing agent in bromine water was decided in favour of molecular bromine by showing that pure hypobromous acid reacts only extremely slowly with glucose.

A mechanism compatible with all the experimental findings involves the anion of glucose in the rate-determining step at all except extremely low values of pH.

This mechanism agrees well with that proposed for the oxidation of other organic compounds[3-5].

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Twelfth Session, Wednesday morning 21.10.59   Chairman: Y. Hirshberg
Physical Chemistry

Dielectric properties of adsorbate-adsorbent systems at low surface coverages

D. Fiat, M. Folman and U. Garbatski, *Department of Chemistry, Technion–Israel Institute of Technology, Haifa*

The existing work on the dielectric properties of vapours and gases adsorbed on solide was performed mainly under experimental conditions which did not allow a

more precise analysis of the results obtained at low surface coverages[1,2,3,4]. The main purpose of this work was to investigate the region of low surface coverages where the absence of adsorbate-adsorbate interactions may greatly facilitate the interpretation of the experimental results.

The measurements were performed with a highly precise capacitance meter of high stability and an accuracy better than 0.001 $\mu\mu$f. This enabled measurements to be made at surface coverages as low as $\Theta = 0.005$.

The dielectric properties of NH_3 adsorbed on porous "Vycor" high silica glass were measured. The surface area of the porous glass plate was 190 m²/g as obtained from B.E.T. measurements at liquid air temperatures, using argon as adsorbate.

The change in capacity ΔC of a condenser containing the adsorbent was measured as a function of the amount adsorbed. From the results obtained the dielectric constants of the adsorbate were calculated, using various "mixing" formulae, on the assumption that the adsorbent remains unperturbed.

The plots show that the dielectric constant ε_a of the adsorbate is a function of surface coverage.

At low surface coverages ε_a increases steadily with the amount adsorbed; this indicates that the orientational freedom of movement of the adsorbate is increased due to the heterogeneity of the surface of the adsorbent.

At still higher coverages, the slope of the ε_a versus amount adsorbed curve changes and at about $\Theta \approx 0.6$ a decrease in ε_a is evident. This may be due to the beginning of interactions between the adsorbate molecules.

Together with the low surface coverage hysteresis in the adsorption isotherms, a hysteresis in the ΔC versus Θ curves was found. This phenomenon confirms previous results where the existence of two different sites of adsorption which differ in energy was shown[5] (this was inferred from the infrared spectra of the adsorbate-adsorbent system). This difference in energy causes a different distribution of the adsorbate molecules between the existing sites for the same amounts adsorbed on adsorption and on desorption.

Time effects in the ΔC versus t curves were observed indicating a redistribution of the adsorbate molecules, before final equilibrium is reached[6] (parallel to previous results).

Finally, comparison of the results obtained at different temperatures for equal surface coverages Θ reveals that the freedom of orientational movement is increased at higher temperatures.

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Infra-red and length change studies in adsorption on porous silica glass

M. FOLMAN* AND D. J. C. YATES**, *Department of Colloid Science, Cambridge University, England*

Expansion-contraction effects in a porous silica glass adsorbent due to adsorption of water and methyl alcohol were studied by interferometric technique and explained by means of infrared spectroscopy[1].

Recent work has shown that the contractions of a rigid porous glass adsorbent when various polar molecules are adsorbed is due to hydrogen bonding between these molecules and the OH groups present on the surface of the adsorbent. Moreover, the magnitude of these contractions could be related to the strength of the particular hydrogen bond formed[2]. On this basis it would be expected that a water molecule which is capable of hydrogen bonding with the surface OH groups would also cause a contraction on adsorption. This is not the case[3]. With water, only an expansion was found, whereas methyl alcohol showed an expansion-contraction curve of the form of that for adsorbates giving hydrogen bonding with the "free" OH surface groups of the adsorbent. This difference in the length change characteristic of adsorption between the two hydroxyl-containing adsorbates is explained by the fact that with adsorbed water no hydrogen bond is formed between the free surface OH groups and the water molecule at the low surface coverages studied, although this molecule is hydrogen bonded to other sites of adsorption. The infrared spectrum of the adsorbed methyl alcohol indicate that this molecule does give hydrogen bonding with the surface OH groups.

Time effects due to redistribution of the adsorbate molecules between the existing sites of adsorption were observed using both methods.

On the basis of spectroscopic data, the possible configurations of the two adsorbates on the surface are discussed.

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The relationship between water content and water partial vapour pressures in solute–water–solvent systems. A new method of determining vapour pressures

A. BANIEL, R. BLUMBERG AND L. GONEN, *Israel Mining Industries Laboratories, Haifa*

In solute–water–solvent systems, the relationship between water content and water partial vapour pressure (w. p. v. p.) for any given solvent can be represented by a series of isotherms. At a given temperature the w. p. v. p. is uniquely determined by

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the water content. If a system is selected in which the solvent phase contains only negligible amounts of solute and the aqueous phase only negligible amounts of solvent, the water content of the solvent phase is a measure of the w. p. v. p. of the aqueous solution in equilibrium with it. This relationship permits the immediate deduction of the w. p. v. p. of an aqueous solution from the knowledge of water content in the solvent, which is simple to determine.

The systems n-hexanol-electrolyte-water, and octane-2-ol-electrolyte-water, were selected as reference systems, and the water content of the solvent phase accurately determined at 20 °C and 40 °C for a series of aqueous solutions of known w. p. v. p. At each temperature there is a straight-line correlation between w. p. v. p. and water content of solvent for a definite range of vapour pressures. These correlations can serve as a simple method for determining w. p. v. p. of aqueous solutions, particularly in the neighbourhood of ambient temperatures.

On the coagulation of aerosols

S. E. WEINSTOCK, *Ministry of Defence*

Aerosols are colloidal systems of liquid or solid particles dispersed in a gas. Their stability, as measured by the rate of decrease of particle concentration is rather low compared to colloidal systems in which the continuous phase is a liquid.

The theoretical basis for the kinetics of coagulation of sols under ideal conditions was formulated by Smoluchowski[1,2]. His final equation for the rate of coagulation may be written in the form:

$$- \frac{dn}{dt} = K_s \, n^2 = \frac{4kT}{\eta} \, n^2$$

where: η = viscosity of the continuous phase

n = numerical concentration in particles/cc

k = Boltzman's constant

T = temperature.

For air at 293 °K, $K_s = 1.77 \times 10^{-8}$ cc/min.

During the last 30 years, a great deal of experimental work was carried out on the problem of coagulation of aerosols, but different results were obtained for K_s. It was supposed that this was a direct consequence of the use of aerosol systems which did not comply with some of Smoluchowski's basic assumptions.

The aim of this work was to re-examine the applicability of Smoluchowski's coagulation rate equation to an "ideal" aerosol, taking proper account of other loss effects than collision between the particles. As an ideal system closely conforming to Smoluchowski's assumptions, a mono-dispersed slightly charged liquid aerosol was chosen. The major advantage inherent in liquid aerosols is the conservation of spherical shape and bulk density both in the primary particles and the aggregates. Di-

octyl-phthalate (DOP) was selected as the dispersed phase because of its extremely low vapour pressure. Errors due to evaporation were thus eliminated.

A series of experiments was carried out with particle sizes in the range of $0.50\mu <$ $r_o < 0.56\mu$, with a standard deviation from the mean of about 10%. The average value for K_s obtained was: $K_s = 2.10^{-8}$ cc/min with a S.D. from the mean of about 10%. Taking into account the accuracy of the experimental technique employed, the agreement with Smoluchowski's theoretical value is highly satisfactory.

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Thirteenth Session, Wednesday morning 21.10.59   Chairman: B. KIRSON
Analytical Chemistry

Rapid determination of aluminium oxide in silicates

WOLF BODENHEIMER AND MOSHE GAON*, *Geochemistry Division, Geological Survey of Israel, Jerusalem*

The rapid method of Shapiro and Brannock[1], based on the spectrophotometric determination of Parker and Goddard[2] and using alizarin red-S and calcium ions, has two main disadvantages:

1. A correction must be made for the interference of titanium oxide, which necessitates a preliminary determination of titanium oxide.

2. The interference of iron oxide must be eliminated by the addition of more reagents, which complicates the procedure.

The method has been changed so that the melt of the sample in sodium hydroxide in a nickel crucible is dissolved in water, boiled with two drops of hydrogen peroxide and filtered into a measuring flask. Iron oxide and titanium oxide are retained in the precipitate, together with the nickel oxide which through the addition of hydrogen peroxide does not coprecipitate aluminium oxide. A standard solution is prepared from aluminium metal, the reagents being added in twice the strength prescribed by Shapiro and Brannock[1], which speeds up the final development of the colour.

Table I shows results obtained by the new method with eight samples analysed in succession, as compared with those obtained by the classical method.

TABLE I

| New method (%) | 15.16 | 15.01 | 12.91 | 15.42 | 12.62 | 11.79 | 18.25 | 12.59 |
| Classical method (%) | 15.33 | 15.12 | 13.25 | 15.68 | 12.73 | 11.96 | 18.23 | 12.76 |

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The determination of trace amounts of gold in rocks, soils and water via carbon adsorption

A. ALON, M. HEITNER-GRYNBAUM AND B. PASCHKES*, *Israel Mining Industries Laboratories*

In carrying out a program of geochemical survey by the Israel Mining Industries, anomalies of gold were encountered. Although a variety of methods had been applied for the microdetermination of gold, including polarographic, chromatographic, colorimetric and mercury amalgamation procedures, it became essential to have a method at hand for critical samples whereby the gold could be determined by weighing it as the pure metal.

Determination by direct fire assay had certain disadvantages, namely, the type of flux to be used was dependent on the composition of the rock to be assayed and, owing to the wide variety of samples, lengthy analyses would have been required to determine this; for rock containing less than 1 ppm of gold, inconveniently large aliquots would have been necessary.

A uniform treatment was sought which could be applied irrespective of the composition of the rock and would permit determination of 0.1 ppm of gold in the sample. It was decided to try activated carbon as a collector of gold from strongly acid solutions.

Fifty to two hundred grams of finely ground sample were leached with 1–2 liters of dilute aqua regia ($\sim$ 2 N) or with hydrochloric acid ($\sim$ 2 N) saturated with bromine. After decantation, the leach liquor was treated with 1 g activated carbon and filtered. The carbon was then washed free of Cl^-, dried, scorified with litharge, and cupelled; the cupel bead was parted and annealed if necessary and finally weighed on a microbalance. Large concentrations of metal ions like Cu, Fe, Al, Mn, Ca, Mg, K and Na in the acid solution did not interfere.

Recovery was 80% or better.

The method has been applied to rocks, soils and mineral waters. The behaviour of noble metals other than silver has not been investigated.

Rapid volumetric estimation of sulfate content of cement by the barium chromate method

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The sulfate content of Portland cement is limited by standard specifications because

of the detrimental effect of an excess of sulfate upon the quality of the product. Natural gypsum is added to and interground with cement clinker in order to regulate the setting and hardening of the cement. A close and rapid control on the addition of gypsum is therefore required. Existing analytical methods are either time-consuming and laborious or require instruments. Therefore the barium chromate method was reexamined for this purpose. A study was made of the extent and character of interference of aluminium, iron, calcium and magnesium ions. From these and other relevant observations a simple method was evolved, employing an empirical reagent solution of barium chloride and potassium chromate in 2 N HCl with the chromate in excess of stoichiometry. After addition of a measured amount of this solution to a hydrochloric acid solution of cement, neutralisation and filtration, the chromate content in an aliquot of the filtrate is titrated with standard ferrous solution on barium diphenylamine sulfonate as indicator. A blank is obtained for a cement of known low sulfate content and from the difference of both titrations the sulfate content of the unknown is calculated. A single determination takes 1/2 hour and six samples may be analysed simultaneously in 2 hours. The method has been in use for 3 years and excellent agreement is found with check determinations by the standard ASTM method.

Fourteenth Session, Wednesday morning 21.10.59   Chairman: E. D. BERGMANN
Physical Chemistry

The isotopic exchange of oxygen between uranyl ions and water

M. ANBAR* AND S. GUTTMANN, *The Weizmann Institute of Science, Rehovoth*

The isotopic exchange of oxygen between uranyl ions and water was investigated in a wide range of uranyl ion concentrations (0.004–2.0 M) and pH values (0.4–5.0) in presence of various ions, including acetate, nitrate, fluoride and ferrous.

A large decrease in the rate of oxygen exchange was observed upon increase of the uranyl ion concentration. Increasing the uranyl nitrate concentration fiftyfold *slowed down* the rate of exchange by a factor of one thousand.

Fluoride ions were found to slow down the rate of exchange considerably. An equimolar fluoride concentration slowed down the rate of exchange by a factor of about 20.

Hydrogen, acetate, ferrous and nitrate ions were found to have little effect on the uranyl nitrate–water exchange.

Further experiments with uranyl perchlorate are in progress.

A mechanism explaining the strong effects of uranyl and fluoride ion concentrations on the oxygen exchange is presented.

The action of hydrogen atoms on the ferro-ferricyanide system

GIDEON CZAPSKI* AND GABRIEL STEIN, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

In previous papers[1,2,3] it was shown that hydrogen atoms produced in an electrodeless discharge act as oxidising agents in acid solutions. The assumption of intermediate formation of H_2^+ ion[4] was found to be consistent with the results.

In the present work the action of H atoms on the ferro-ferricyanide system was investigated. In this system reduction was found to prevail even in fairly acid solutions. The absence of oxidation is explained by the assumption that in the present case the reduction process is by way of a fast electron transfer, whilst in the case of the ferro-ferri ion system, for example, it is by way of a slower group transfer.

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The photochemistry of ferrous ions in aqueous solution

JOSHUA JORTNER AND GABRIEL STEIN*, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

The dependence of the quantum yield on the pH, light intensity, ferrous and ferric ion concentration and presence of O_2 was investigated. The quantum yield was found to depend on the pH. A reaction mechanism is proposed which accounts for the role of H^+ ions in photochemistry and elucidates the intermediate steps between light absorption and photochemical reaction. Comparative experiments with light and heavy water are discussed.
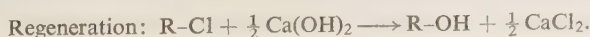
Fifteenth Session, Wednesday afternoon 21.10.59   Chairman: H. HEYMAN
Industrial Chemistry

The conversion of potassium chloride to potassium hydroxide with the aid of anion exchange

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Potassium chloride is converted to potassium hydroxide according to the following reactions:

$$\text{Loading: } KCl + R\text{-}OH \longrightarrow KOH + R\text{-}Cl$$

$$\text{Regeneration: } R\text{-}Cl + \tfrac{1}{2} Ca(OH)_2 \longrightarrow R\text{-}OH + \tfrac{1}{2} CaCl_2.$$

R is the skeleton of a strongly basic anion exchanger. The ion-exchange takes place in aqueous solution, that of the calcium hydroxide being saturated.

The degree of separation between the hydroxide formed and unconverted chloride is determined by plotting effluent concentration versus effluent volume. Graphical integration of the curves yields the amount of production.

The experiments attained a cyclic equilibrium in which the number of milliequivalents of chloride introduced during loading was equal to that liberated during regeneration.

Numerical results under optimal conditions are given.

The development of the dicalcium phosphate process

A. STRAUCHEN, *Fertilizers and Chemicals, Haifa*

There are two main commercial dicalcium phosphate grades: 1. fertilizer grade and 2. feed grade. The feed grade dicalcium phosphate must be substantially free from fluorine. Starting from phosphate rock and/or green phosphoric acid, a defluorination step must be introduced into the production process, which always leads to appreciable P_2O_5 losses.

A one-stage process worked out by F & C, now in use, succeeded in reducing the losses of P_2O_5.

A new double-stage process devised by the F & C chemical staff will increase the P_2O_5 recovery, simultaneously reducing the acid consumption and saving CaO.

A third process also developed by our staff leads to almost 100% P_2O_5 recovery in a combined process, where feed-grade dicalcium phosphate will be obtained together with the production of fertilizer-grade dicalcium phosphate or high grade enriched phosphate.

This last process will be of special importance if cheap HCl is made available in great quantities, as a by-product of processes under consideration:

$$MgCl_2 . 6aq. \longrightarrow 2 HCl + MgO + 5 H_2O$$

$$KCl + H_3PO_4 \longrightarrow HCl + KPO_3 + H_2O$$

Short-cuts in research through the empirical study of literature: The adsorption of polar molecules on surfaces of minerals

A. BANIEL[*] AND A. MITZMAGER, *Israel Minning Industries Laboratories, Haifa*

The separation between particles of minerals in the fine-powder range (1–30 microns) is a basic technological problem, the solution of which should contribute to the world's supply of minerals. Separations in the fine-powder range must rely on differences in surface properties. Consequently selective modification of surfaces through the adsorption of suitable reagents is of the greatest importance. No

comprehensive and systematic work on this subject has been published to date. There are, however, numerous published studies pertaining to flotation, cosmetics, corrosion, and solid-state investigations, but these represent such a variety of approaches that occasionally there is a complete absence of common concepts. The available data were collected in our laboratories and correlation experiments made in an effort to define the scope of the whole field, to weigh the relative importance of the information collected and the possibilities of increasing it by filling in previous studies and to derive new directions of study by a critical evaluation of the material. Considerable new knowledge was gained (part of it fully established and the rest of various grades of probability) that could not be obtained by the customary literature search. The whole work consisted of an empirical study in which only results obtained in previous researches were manipulated. This illustrates the economy in manpower and time obtainable when the treasure of chemical literature is approached with the philosophy usually applied to experimental investigations in the laboratory.

Water problems at Timna copper plant

A. MITZMAGER*, A. BANIEL, J. GAILIS AND J. MIZRAHI, *Israel Mining Industries Laboratories, Haifa*

The Timna copper plant daily treats 1500 tons of ore containing an average of 1.4% Cu by sulphuric acid leaching, counter-current washing in thickeners, and cementation, the product being cement copper averaging 80% Cu. The main reactions are:

$$(Mineral)\ CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$CuSO_4 + Fe \longrightarrow Cu + FeSO_4.$$

The whole process requires four cubic metres of water for each ton of ore. One m³ per ton is discarded with the tailings, and three m³ are evacuated as barren solution after cementation, containing the following ions (g/l): Fe^{++}, 4.5; Cu^{++}, 0.07; Al^{+++}, 0.4; Ca^{++}, 0.56; Mg^{++}, 0.38; $PO_4^{\equiv}$, 4.8; and also Mn^{++}, Na^+, K^+, $SO_4^=$ and Cl^-. The *p*H is approximately 2.8.

Treatment of this effluent is necessary for two main reasons:

1. Pollution of underground water with undesirable ions.
2. Recovery of water for re-use.

Direct recirculation of this effluent to the washing circuit involves some technical complications due to the presence of ferrous and phosphate ions in the effluent and MnO_2 in the ore.

Of the several methods investigated for removal of ferrous ions from the barren solution, two were selected for laboratory and pilot plant experiments. These were:

1. Neutralization to *p*H 4–5 with ground limestone in the presence of air as oxidant and precipitation of the iron as ferric hydroxide.

2. Neutralization with lime to pH 6.5 and precipitation of iron as ferrous hydroxide.

The selection of one of these methods for practical use will be dictated by economic considerations.

Magnesium bromide from brines of the Dead Sea

R. BLUMBERG*, A. BANIEL AND J. MASHAL, *Israel Mining Industries Laboratories, Haifa*

A process has been elaborated for the selective extraction of magnesium bromide from Dead Sea end-brine[1]. This end-brine, which is the normal local source of elementary bromine, contains some 10–12 g Br^-/1 and over 300 g Cl^-/1. In addition it contains 40–50 g Ca^{++} and approximately 90 g Mg^{++}/1. From this brine, by a suitable series of liquid-liquid extraction operations using n-butanol as extracting solvent, a pure magnesium bromide solution uncontaminated by chloride or calcium ions is obtained in a concentration of 100 g Br^-/1. This pure solution can form the starting point for a bromide industry.

The process is in the stage of pilot-scale development, since preliminary cost analyses have shown it to possess attractive economic possibilities.

In the course of the laboratory investigations, interesting information was obtained on the selective extraction of molecular species from brines by alcohols.

REFERENCE

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Sixteenth Session, Wednesday afternoon 21.10.59   Chairman: D. GINZBURG
Physical Chemistry

The photochemistry of aqueous solutions of benzene

ISRAEL LOEFF* AND GABRIEL STEIN, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

In previous work[1,2,3] it was shown that aqueous solutions of benzene irradiated with X, γ or α rays in the presence of O_2 yield muconic dialdehyde, and thus aromatic ring opening occurs. We have shown[4] that mucondialdehyde is a primary product and that a single radiation step is required for its formation. Similar views have been expressed recently[5].

In the present work it was shown that similar ring opening takes place when such solutions are irradiated with UV light of 2537 Å. However, in this case, where excited benzene molecules are the primary intermediates, the pH dependence and the ratio of dialdehyde, phenol and catechol are different from the case of ionizing radiations. Experiments in the absence of O_2 led to the formation of catechol and phenol, but

not mucondialdehyde. A mechanism involving the interaction of the first singlet excited state of benzene with water or O_2 is suggested. Above 2900 Å no photochemical changes could be observed.

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Temperature dependence of the rates of photoisomerisation of spiropyrans

R. HEILIGMAN, Y. HIRSHBERG AND E. FISCHER *Laboratory of Photochemistry and Spectroscopy, The Weizmann Institute of Science, Rehovoth*

The rates of photoisomerisation of spiropyrans in a non-polar solvent were found to depend strongly on the temperature. This effect is particularly pronounced for the photo-conversion of the coloured modification into the colourless one by the action of light in the visible region of the spectrum. The observations for two compounds dissolved in methyl-cyclohexane/petrolether are summarized in the table, which gives values for $\tau_{\frac{3}{4}}$ (the time of irradiation with visible light needed to reduce the concentration of the coloured modification to 3/4 of its original value).

Temperature °C	$\tau_{\frac{3}{4}}$ for compound (I), minutes	$\tau_{\frac{3}{4}}$ for compound (II), minutes
–90	0.15	2
–120	14	13
–135	>120	33
–160	immeasurable	>120

The effect is not due to increased viscosity of the solvent mixture, which is still very low even at –160°. No similar effect was observed in alcoholic solutions. Possible explanations of the above phenomenon are: (*a*) a potential barrier exists between the *excited* states of the coloured and the colourless modifications; (*b*) the light-induced isomerisation includes a *thermal* step (such as stereo-isomerisation of the various possible isomers in the ground state), which depends on the temperature like regular thermal processes.

REFERENCE

1. HIRSHBERG, Y. AND FISCHER, E., 1954, *J. chem. Soc.*, 297, 3129.

Equilibria at low temperatures in solutions of the coloured modifications of spiropyrans

R. HEILIGMAN, Y. HIRSHBERG AND E. FISCHER, *Laboratory of Photochemistry and Spectroscopy, The Weizmann Institute of Science, Rehovoth*

Experiments in the temperature range between 90° and 180° Kelvin showed that the spectrum of the coloured modifications of certain spiropyrans[1], as well as the effect of temperature on the spectrum of these compounds, are determined to a great extent by the nature of the solvent (Figures 1, 2, 3).
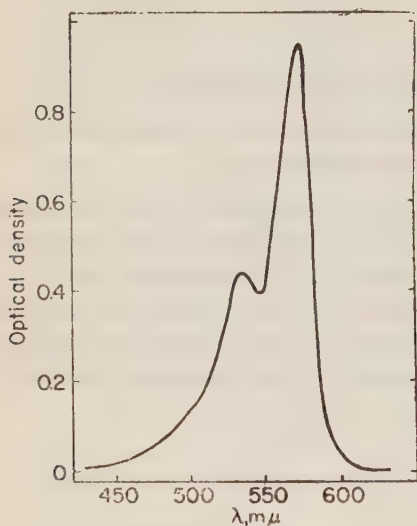
Figure 1
Absorption spectrum of the coloured modification of 1,3,3-*trimethyl indolino-naphtho spiropyran,* in ethanol/methanol, 3mg/l, at –100°C
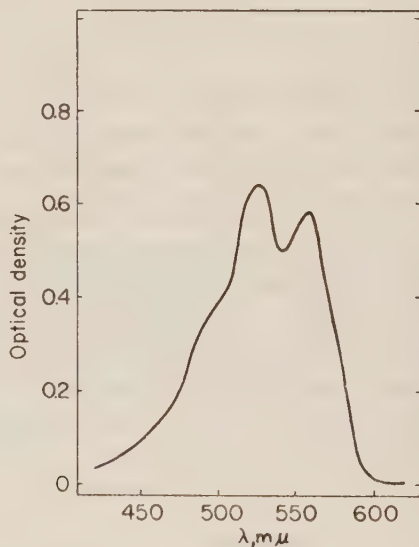
Figure 2
Absorption spectrum of the same compound in methyl-cyclohexane / petrol ether, 3mg/l, at –100°C
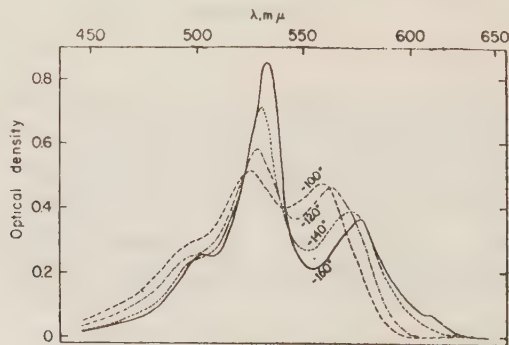
Figure 3
Same as in Figure 2, at different temperatures

These phenomena point to the coexistence of several interconvertible stereoisomers of the coloured modification in its solution, the relative concentrations of these stereoisomers, S_1, S_2, S_3, S_4, being determined by highly temperature-dependent equilibria:

$$S_1 \leftrightharpoons S_2 \leftrightharpoons S_3 \leftrightharpoons S_4$$

In an alcoholic solution one of the stereoisomers appears to be stabilised against the others by association with the molecules of the solvent.

REFERENCE
1. HIRSHBERG, Y. AND FISCHER, E., 1954, *J. chem. Soc.*, 297, 3129.

Low temperature thermochromism of some coordination compounds

YEHUDA HIRSHBERG , *Laboratory of Photochemistry and Spectroscopy, The Weizmann Institute of Science, Rehovoth*

Dilute alcoholic solutions of uranyl salts with either diphenyl-carbazone or 1,5-diphenyl-carbohydrazide are practically colourless and do not absorb in the visible range at room temperature. On cooling, the mixtures develop a red colour and a broad band, peaked at about 510 mμ, appears in the absorption spectrum. The red colour and the absorption band in the visible region are enhanced on cooling. At about 118 °K two maxima appear instead of the former single one.

The effect is reversible, with a definite band height attained at any temperature.

The phenomenon just described can be repeated many times with the same solution mixtures.

It seems that low temperatures in these cases favour the formation of the coloured coordination compounds, even at very low concentrations. The above phenomena represent a temperature-dependent equilibrium between the chelate and its components.

Irradiation of the solutions with light at 300 + 313 mμ results in the reversion of the chelates to their original colourless non-chelated mixture of components. Neither visible light, although this is absorbed by the coloured chelates, nor the 365 mμ group of the mercury arc have any effect on them. Dilute mixtures of mercuric iodide and diphenyl-carbazone were also found to form similar reversible coloured coordination compounds on cooling as described above.